FACTORS CONTROLLING THE ABUNDANCE AND CARBON ISOTOPIC COMPOSITION OF LAND-PLANT DERIVED COMPOUNDS IN CRUDE OILS

by

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ABSTRACT

This thesis describes a study in petroleum geochemistry and specifically of the application of land-plant derived hydrocarbons to elucidating source matter type, depositional environment and thermal maturity of crude oils. Large volumes of petroleum have been generated from land-plant organic matter in many parts of the world, but especially in the Tertiary deltaic provinces of the USA, Canada, Africa, Southeast Asia, Australia and New Zealand. Compared to oils from other regions, these oils have a relatively complex pattern of biomarkers or molecular fossils, a feature reflecting the diversity of deltaic depositional environments and the advanced state of plant evolution during late Mesozoic and Tertiary time. The molecular and carbon isotopic composition of these oils is useful in identifying the character of their source beds and also in understanding the conditions that give rise to oil-prone sediments generally.

Despite their widespread occurrence in oils and sediments, land-plant biomarkers have been used less frequently than compounds of algal origin as markers for source, depositional environment and thermal maturity. The present work sets out to extend the range of land-plant biomarker and isotope tools available to the petroleum geochemist and to provide a firmer foundation for some of the existing tools. A systematic study of the biomarker and n-alkane carbon-isotope composition of a set of late Mesozoic/Tertiary-age oils was carried out as a preamble to more focussed investigations. A comparison of the biomarker and n-alkane isotope data showed that parameters such as the oleanane/hopane ratio overestimate the higher plant contribution to marine deltaic oils. The abundance of bicadinane isomers was found to be much more variable than that of the oleananes, probably because of their close association with the highly resinous, dipterocarp hardwoods of Southeast Asia. However, small amounts of bicadinanes were found in an oil from outside the paleogeographic range of the dipterocarp family, indicating a more general source. Retention indices based on the

regular hopane series were calculated for the main bicadinane and methyl bicadinane isomers and for a group of oleanoid triterpanes.

Source rock depositional setting proved to be the primary control on the shape of the n-alkane isotope profile, with negatively sloping curves being characteristic of fluvio-deltaic and marginal lacustrine oils and flat or positively sloping curves typical of marine oils. The difference is probably related to the bacterial reworking of higher plant matter in the fluvio-deltaic environment. A slight isotopic anomaly at n-C$_{17}$ correlates with the abundance of algal-derived steranes and may indicate a minor marine contribution to the source of an fluvio-deltaic oil. A study of sediments from the South Sumatra Basin and New Zealand showed that the n-alkane isotope profile is determined mainly by source matter type and is little influenced by thermal maturity or depositional environment.

Based on the results of the work described above, three aspects were chosen for further examination. These were: a) the factors controlling the carbon isotopic composition of n-alkanes and of resin-derived compounds in terrigenous oils; b) the influence of source, maturity and biodegradation on the abundance of bicadinanes, especially the effect of maturity on the isomer distribution, and c) the factors controlling the abundance of oleananes and rearranged oleananes in oils and Ancient sediments, especially the role of depositional environment.

A preliminary study using sediments from the Visayan Basin (Philippines) showed the bicadinane isomeric distribution to be sensitive to maturity. This suggested new maturity parameters which would be resistant to even severe biodegradation and largely immune to interference from diagenetic effects. A more detailed study of a marine-fluvio-deltaic depositional sequence from the South Sumatra Basin confirmed that the maturity indices based on bicadinanes and aromatic analogs were less subject to non-maturity influences than those based on the steranes and aromatic hydrocarbons. The values obtained for the bicadinane indices were compared with the

maturity required for oil generation as estimated by kinetic modelling and with conventional maturity indicators such as sterane epimerisation and the methyl phenanthrene index. Values for several of the indices were also measured for 17 Tertiary-age oils from Southeast Asia, Papua New Guinea, New Zealand and Australia. The main bicadinane maturity indicator (BMI-1) continues to change into the oil window and hence is useful in ranking the relative maturity of oils as well as sediments. Values of BMI-1 for two oils having unusually low sterane maturities were found to be normal and, in the light of this observation, the conventional explanation for low sterane epimerisation of many Tertiary-age oils was critically evaluated.

The oleananes, as markers for the angiosperms, provide valuable source and age information when present in an oil. Nevertheless, their abundance is not quantitatively related to the land plant input and indeed their presence results from a small "leak" in diagenetic processes leading primarily to aromatic oleanoids. Evidence is presented that contact of plant matter with seawater during early diagenesis enhances the expression of oleananes in a mature sediment or oil. Oleananes are absent or present at very low concentrations in samples from the base of an Eocene coal seam affected by post-depositional seawater intrusion. However, their abundance increases toward the top of the seam in correlation with % organic sulphur, dibenzothiophene/phenanthrene and the homohopane index. Similarly, in deltaic sediments from the South Sumatra Basin, oleanane/hopane is strongly correlated with indicators of marine influence such as C_{27}/C_{29} steranes and of oxic/anoxic conditions such as the homohopane index. In each case, increasing oleanane abundance is accompanied by a reduction in the extent of aromatisation and, for the South Sumatra Basin, the proportion of A-ring contracted oleananes. An angiosperm-derived Miocene coal from the Philippines, deposited under freshwater conditions, shows abundant aromatic oleanoids but no oleananes. These results show that oleananes need to be used with caution as age and source markers in fluvio-deltaic and lacustrine petroleum systems. On the other hand, their sensitivity to early

diagenetic conditions may make them useful in locating effective source rocks in such systems.

Compounds derived from plant resins are major components of some terrigenous oils. Although recent studies have elucidated the molecular structure of resinites, very little information was available on the carbon isotope composition of resinites prior to the present study. No carbon isotope studies of resin-derived compounds in oils had been performed. Hence, carbon stable isotope analyses were carried out on a set of modern and fossil resins of diverse origins and compound specific isotope analysis was used to characterise individual hydrocarbons in resin pyrolysates and oils derived from resinitic source matter. The results showed that "Class I" resinites derived from gymnosperms are enriched in the heavy carbon isotope compared with the angiosperm-derived "Class II" resinites. Furthermore, both the fossil resinites themselves and individual hydrocarbons derived from them are isotopically heavy compared with modern plant resins. The reasons for these differences and their implications for petroleum geochemical studies are discussed.

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PUBLICATIONS ARISING FROM THIS STUDY

Murray A.P., Summons R.E., Boreham C.J. and Dowling L.M. (1994) Biomarker and *n*-alkane isotope profiles for Tertiary oils: relationship to source rock depositional setting. *Org. Geochem.*, **22**, 521-542.

Sosrowidjojo I.B., Murray A.P., Alexander R., Kagi R.I., and Summons R.E. (1996) Bicadinanes and related compounds as maturity indicators for oils and sediments. *Org. Geochem.*, **24**, 43-55.

Murray A.P., Sosrowidjojo I.B., Alexander R., Kagi R.I., Norgate C.M. and Summons R.E. (1997). Oleananes in oils and sediments: Evidence of marine influence during early diagenesis ? *Geochim. Cosmochim. Acta*, **61**, 1261-1276.

Murray A.P., Edwards D.E., Hope J.M, Boreham C.J., Alexander R. and Summons R.E. (1997). Carbon isotope biogeochemistry of plant resins and derived hydrocarbons. *Org. Geochem.*, **29**, 1199-1214

Murray A.P., Sosrowidjojo I.B., Alexander R. and Summons R.E. (1997). Locating effective source rocks in deltaic petroleum systems: Making better use of land-plant biomarkers. *Proceedings of the IPA/AAPG/APEA symposium on petroleum systems of Southeast Asia and Australasia.*, Jakarta, May, 1997.

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CHAPTER 1:   INTRODUCTION

1.1   Biomarker science and petroleum geochemistry

Petroleum geochemistry is the branch of organic geochemistry concerned primarily with the search for and exploitation of hydrocarbons. At the time of writing the average cost of drilling a hydrocarbon exploration well in Australia is ~ A$10 million and one in seven wells results in a commercial discovery (E.Petrie, Australian Government, Bureau of Resource Sciences, personal communication). Thus the cost of finding a new hydrocarbon accumulation averages A$70 million and any reduction in risk furnished by organic geochemical studies is economically valuable. Fossil fuel related issues are therefore prominent in the field of organic geochemistry, but this does not narrow the scope. Studies in petroleum geochemistry may require forays into the fields of sedimentology, taxonomy, paleobiology, paleogeography, tectonics, oceanography and biochemistry. Furthermore, studies of fossil fuel molecular and isotope characteristics must take account of the wide range of temperatures and pressures found in the geosphere and the fact that even very slow reactions may become significant over geological time.

"Biomarkers" or "molecular fossils" are organic compounds found in petroleum and Ancient sediments and derived from biochemicals found in living organisms (Eglinton and Calvin, 1967; Peters and Moldowan, 1993). Evidence for the relationship between the precursor and fossil molecule can be either structural or isotopic, i.e., the skeleton of the biomarker may resemble that of the precursor with any differences attributable to alteration during senescence or burial (e.g., dehydration, aromatisation) or, the carbon isotopic signature of the molecule may be inherited from that of a known precursor, again with any changes being explicable in terms of known sedimentary processes. The isoprenoid botryococcane (Fig. 1.1) derived

from fresh or brackish water algae, is an example of a compund which shows both structural and isotopic affinity with its precursor, botryococcene (Moldowan and Seifert, 1980; De Leeuw and Largeau, 1993 and references therein). As yet, chemical fossils do not provide the degree of spatial and temporal resolution attainable in conventional paleontology. On the other hand, unlike macrofossils they are present in both sediments and oils and so can be used for oil-source correlation. Biomarkers are routinely used in petroleum geochemistry for the following purposes (Peters and Moldowan, 1993):

(a)   Oil-oil and oil-source correlation.

(b)   Estimating the thermal maturity of an oil or sediment through observation of changes in molecular configuration or abundance.

(c)   Estimating the degree of microbial degradation by virtue of the differing susceptibilty of compound classes and of particular compounds.

(d)   Estimating the distance an oil has migrated from its source bed (this application being far less developed than the others).

Oil-oil and oil-source correlation is carried out in both a specific and general sense. In the former, the molecular and isotopic properties of an oil are used to group it with other nearby oils or with a particular source rock horizon. In the latter, the oil chemistry is interpreted in terms of broad characteristics of the source rock such as the origin of the organic matter present, the lithology of the host rock, the relative availibility of oxygen or reduced sulphur during early diagenesis and the mode of bacterial decay. When applied in this way, biomarker information becomes a predictor not only of the likely source of a particular oil but of the conditions which give rise to oil-prone rocks in the general sense. As such, it is a powerful adjunct to the petroleum systems concept (Bradshaw et al., 1994,1997; Demaison and Moore, 1980) wherein

the development of source rocks is viewed in a tectonic and sequence stratigraphic framework.

Botryococcene
Botryococcus sp. algae

Botryococcane
sediments, oils
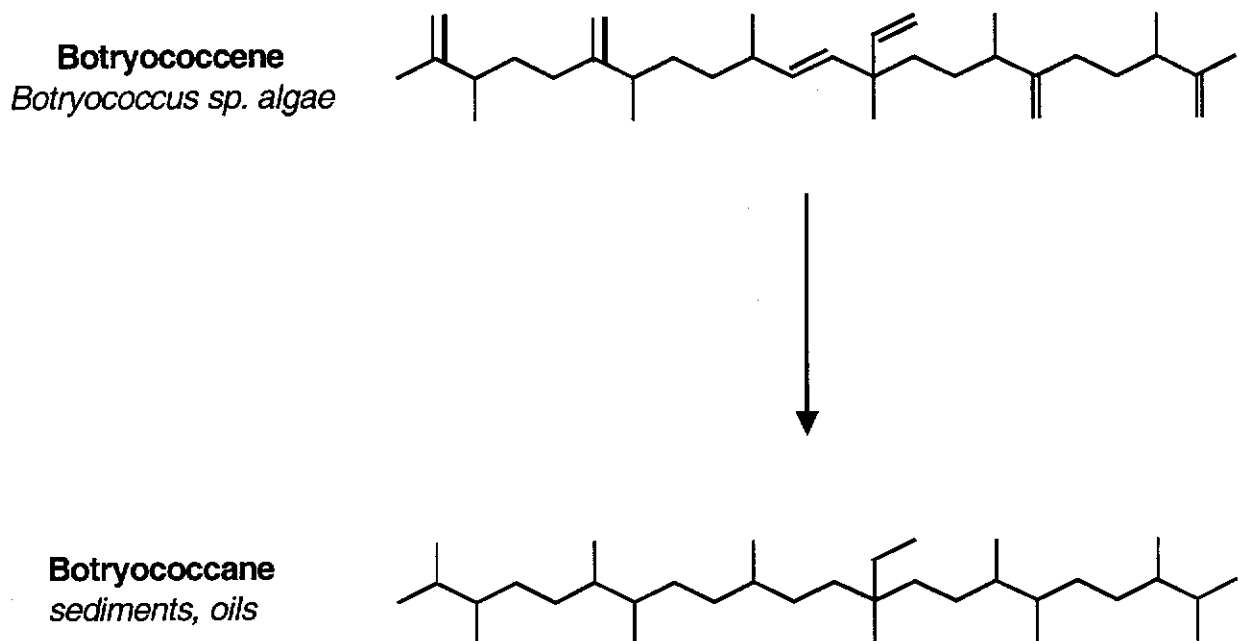
Figure 1.1   Botryococcane is an example of a petroleum hydrocarbon showing a structural affinity with a precursor molecule found in a living organism.

The two main controls on the biomarker composition of an oil are a) the type of organic matter present in its source bed, i.e., the relative contribution of algal, microbial and land plant organic matter, and b) the depositional environment, i.e., all those physico-chemical characteristics such as host rock lithology, water column salinity, oxicity, acidity etc. which determine the mode and extent of chemical and biological alteration during and immediately after deposition (Moldowan et al., 1985; Peters and Moldowan, 1993; Peters et al., 1986). The biomarker profile of an oil is also affected by secondary influences such as the thermal maturity of the source rock at expulsion, in-reservoir maturation, water washing, biodegradation and migration. Indeed, it is not possible to extract source and depositional environment information from biomarker profiles without consideration of

these influences. For example, although the ratio of rearranged to regular steranes in an oil is often used to infer source rock lithology and oxicity/anoxicity in the depositional environment, this ratio is also affected by maturity and by heavy biodegradation. A comprehensive review of the principles and applications of biomarker technology has been presented by Peters and Moldowan (1993).

1.2   The need for further research into land-plant biomarkers

Certain biomarkers in oils are considered characteristic of different primary biomass components. For example, the extended hopanes are derived from precursors in bacterial cell membranes while steranes originate mainly from sterols present in the cells of eukaryotes (Rohmer et al., 1992 and references therein). Early reports suggested that only marine organic matter was oil-prone and that land-plant biomass - so called "Type III" organic matter gave rise mainly to gas (Tissot and Welte, 1984 and references therein). This view has now given way to the realisation that very large quantities of oil have been generated from land-plant organic matter, especially in the deltaic petroleum systems of Africa (Ekweozor and Udo, 1988), Southeast Asia (van Aarssen et al., 1992a; Dzou and Hughes, 1993; Grantham et al., 1983; Hoffmann et al., 1984; Noble et al., 1991; Robinson, 1987), Australia (Alexander et al., 1987,1988; Noble et al., 1985a; Philp et al., 1981; Shanmugam, 1985), New Zealand (Cook, 1988; Czochanska et al., 1988; Killops et al., 1995), South America (Mello et al., 1988) and Canada (Brooks, 1986; Curiale, 1991; Snowdon and Powell, 1982). This realisation is based partly on the almost universal presence in the oils of abundant land-plant derived biomarkers such as long-chain ("waxy") n-alkanes, oleananes, lupanes, conifer derived diterpanes and aromatic hydrocarbons, cadalenes and bicadinanes (Figs. 1.2 - 1.5). Nevertheless, some geochemists (Katz, 1994) do not accept that land-plant matter can be a good source for oil on its own, especially if present as coal, and this emphasises the need for further work on the behaviour and significance of land-plant derived biomarkers.

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In a study of the Lower Cretaceous Aspen Shale (Wyoming, USA), Dahl et al. (1993) concluded that source quality was related to the degree of marine algal contribution, and that this could be inferred from biomarkers. This concept was then used to map source rock quality in the Tertiary Beaufort-McKenzie Delta on the premise that a more marine biomarker pattern in oils (higher relative content of C_{28} and C_{30} steranes) equated to more hydrogen rich source rocks and hence to greater oil potential (McCaffrey et al., 1994). However, numerous studies (see Boreham and Powell, 1993 for a review) have shown that land-plant matter can be just as oil-prone as marine-derived organic matter. Furthermore, in many prolific oil-producing basins, extensive geological and geochemical studies have provided no evidence for a significant contribution of marine organic matter to the source (Cook, 1988; Czochanska et al., 1988; Grantham et al., 1983; Hoffmann et al., 1984; Killops et al., 1995; Noble et al., 1991; Robinson, 1987)

Katz (1994) has suggested that, contrary to the popular view, coals are not a major source of oil in the Indo-Australian region. He argued that coals can generate but not expel oil and stated that:

"conventional lacustrine or marginal marine" source rocks are now known to be present in many coal bearing sequences", and *".. oils often correlate better geochemically with these units than with the coals."*

Miyazaki (1995) used similar reasoning to exclude coal as a potential source of oil in the Bass Basin. He referred to the question posed by Scott and Fleet (1994):

"If oil can be generated from at least some terrestrial organic matter, why do we not see more in reservoired accumulations ?"
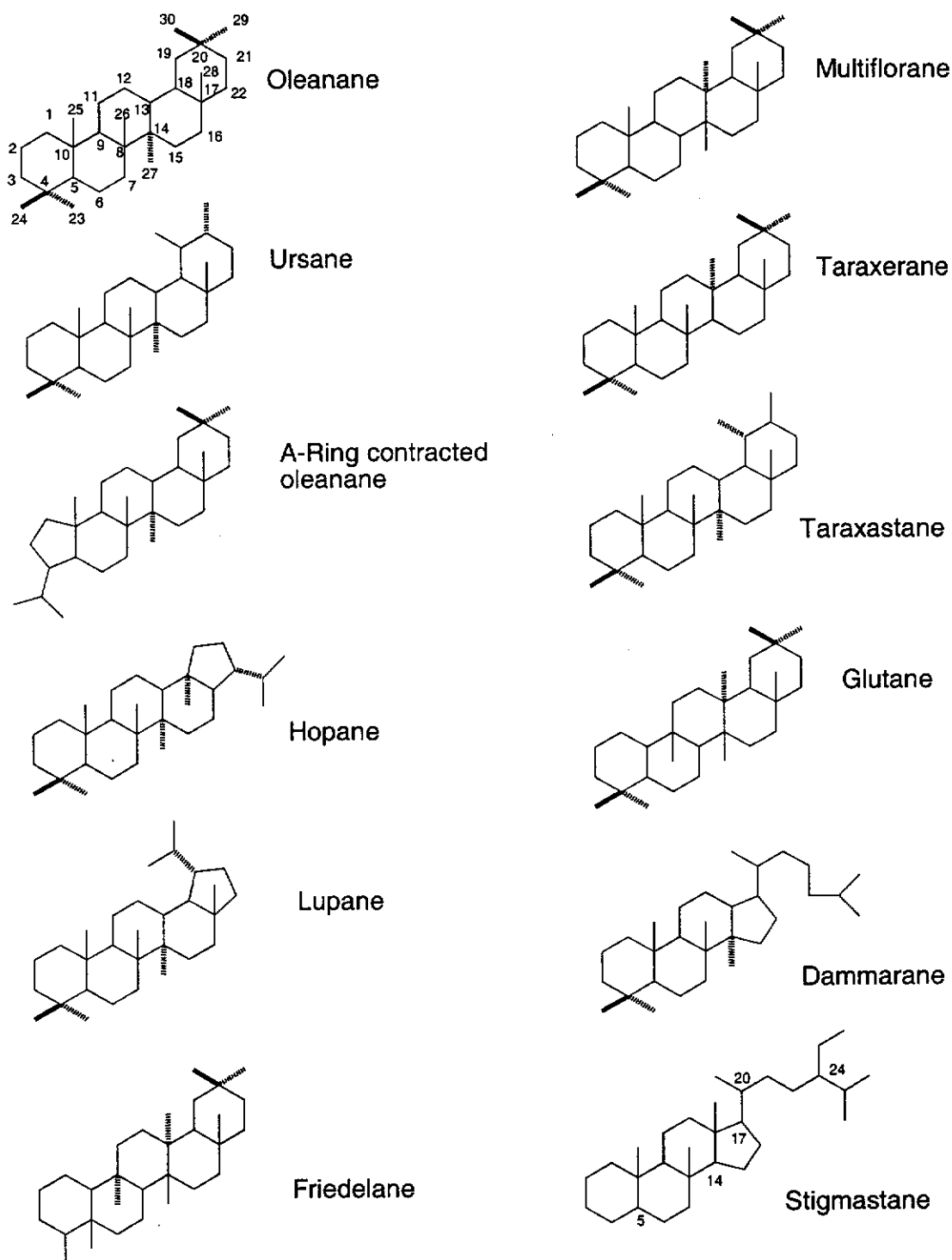
Figure 1.2   Examples of terpenoid skeletons found in land plants and reported to occur in Ancient sediments or crude oils. Most of the natural products are alcohol, ketone, acid or ester functionalised at the 1, 3 and/or 28 positions. Based on Das and Mahato (1983), Rullkötter et al., (1994) and references therein.

Conifer Terpenoids

Labdanoid polymer

Communic acids and communols

Pimaric acids, isopimaric Sandaracopimaric acids, Isopimara-di-enes

Abietic acid

Agathic acid

Podocarpic acid

Phyllocladene

Fossil Molecules

1,2,5-Trimethylnaphthalene

1,7-Dimethylphenanthrene

Phyllocladanes

Bisnorlabdanes

Labdanes

Retene

1-Methylphenanthrene

Isopimaranes, Pimaranes, Sandaracopimaranes

Fichtelite

Figure 1.3   Conifer terpenoids and their hydrocarbon derivatives found in oils and sediments. After Alexander et al. (1992).

Polycadinene

Bicadinanes

Diaromatic
Secobicadinanes

Diaromatic
Secotricadinanes

cis-cis-trans (W)   trans-trans-trans (T)

Cadinanes   Cadalenes   1,6-Dimethylnaphthalene
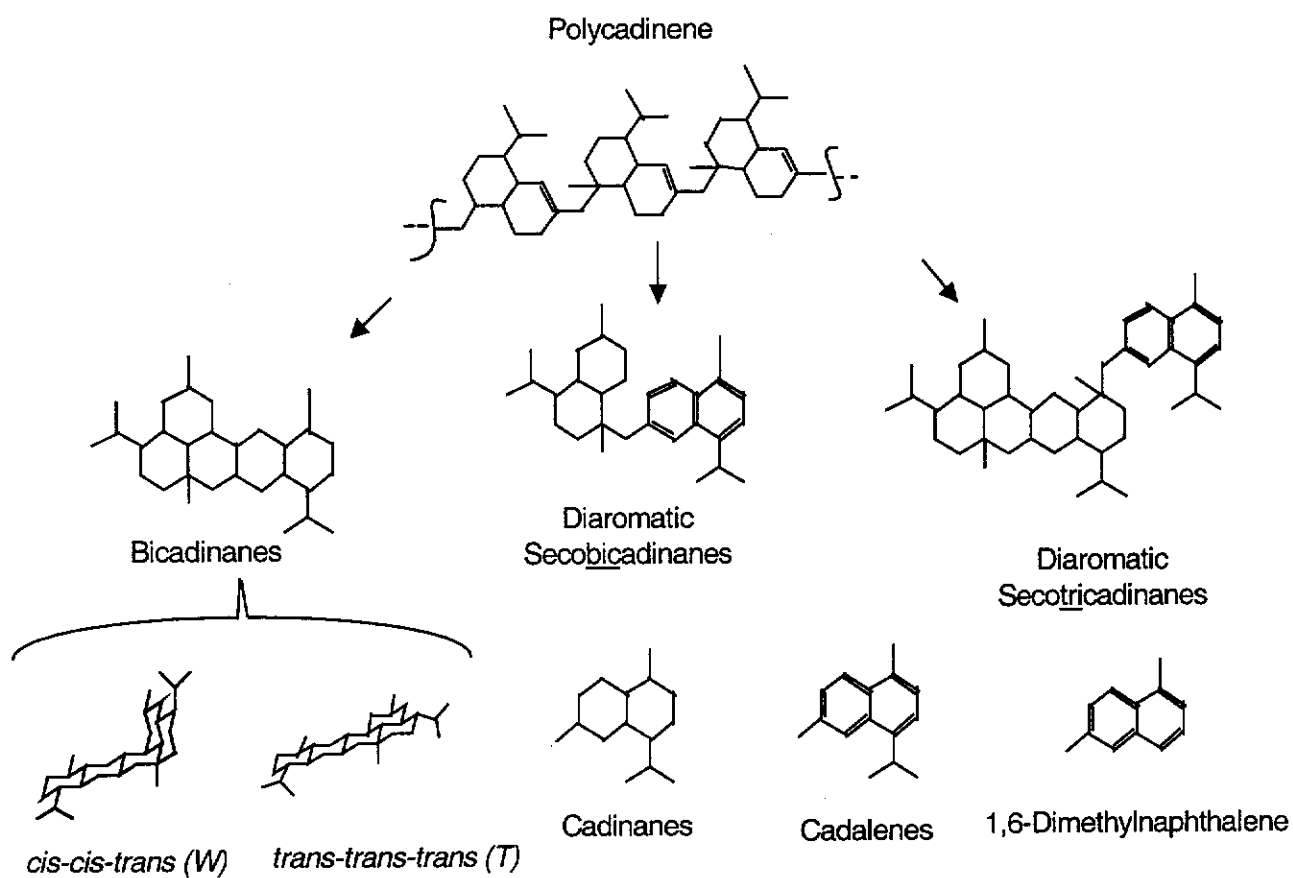
Figure 1.4   Some products of catagenetic dissociation of the plant-resin polymer,
polycadinene.
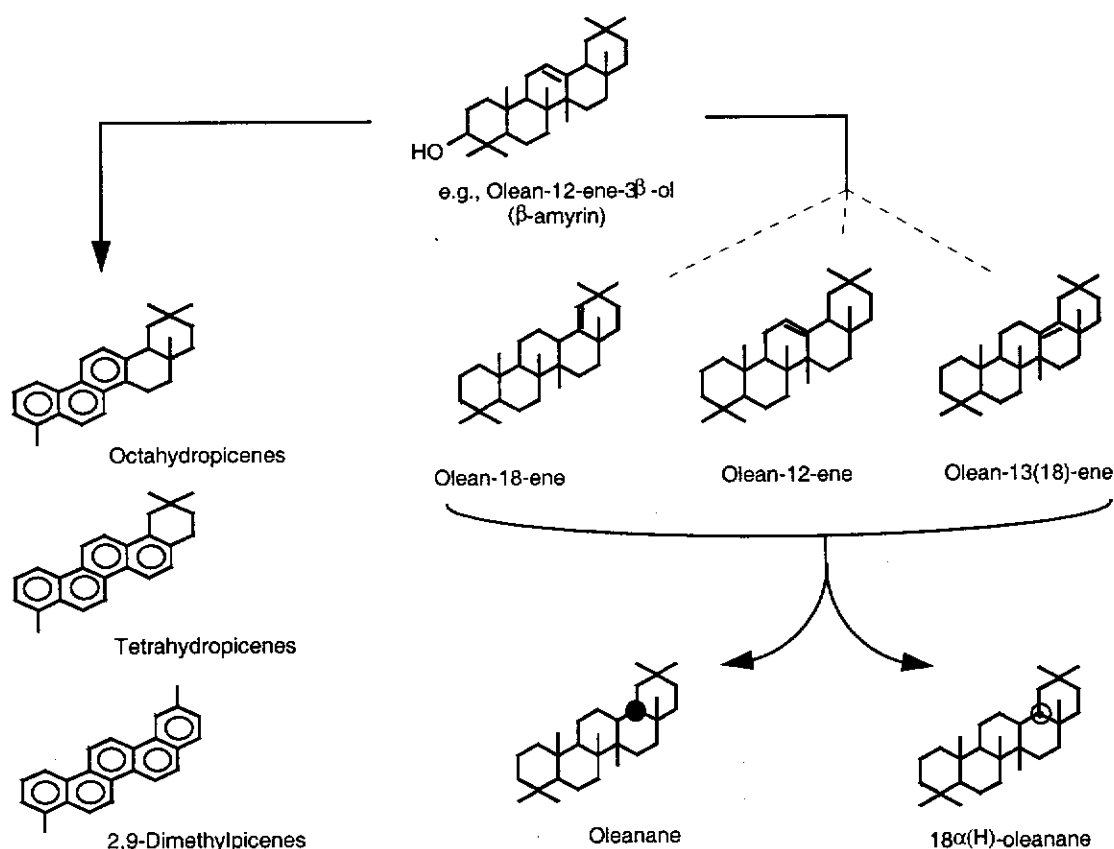
Figure 1.5   Origin of saturated and aromatic oleanoids from (e.g.) β-amyrin type precursors. See Rullkötter et al., (1994) and Stout (1992) for a more complete summary of the origin of oleanoid hydrocarbons.

However, to fully state this conundrum, we must also ask why, if coal is not a source of oil in, e.g., the Gippsland, Taranaki, Arjuna and Kutei basins, how can we account for the volume of oil found there ? In most of these basins, carbonaceous shales of quality and extent sufficient to generate the observed quantities have not been identified despite extensive drilling, often to basement (Cook, 1988; Killops et al., 1995; Noble et al., 1991; Shanmugam, 1985; L. ten Haven, pers. comm.). Nevertheless, the authors of such studies often refer to the source as "coals and carbonaceous shales". Distinction between the lithologies is important, because estimated oil yield will vary by orders of magnitude depending on whether coals are included or excluded from the volumetric equations. Thus, research into the behaviour and occurrence of land-plant biomarkers should aim not only to determine the type of organic matter which has given rise to an oil, but also the environment in which it was deposited - lake, flood plain, paralic swamps,

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proximal or more distal marine sediments (Fig. 1.6). A correct interpretation of the biomarker chemistry of seep or test oils, and it's integration with the sequence stratigraphy, may significantly reduce risk "ahead of the drill". The importance of this is highlighted by the comments of a geoscientist from the Shell company speaking at a conference of the American Association of Petroleum Geologists (Doust, 1994):

"The mechanisms of generation and migration in Far East (Asia and Australasia) Tertiary basins are poorly understood...........however, there is convincing evidence that charge is one the most dominant parameters in determining basin and play prospectivity and that source rock development is both local and strongly environment related"
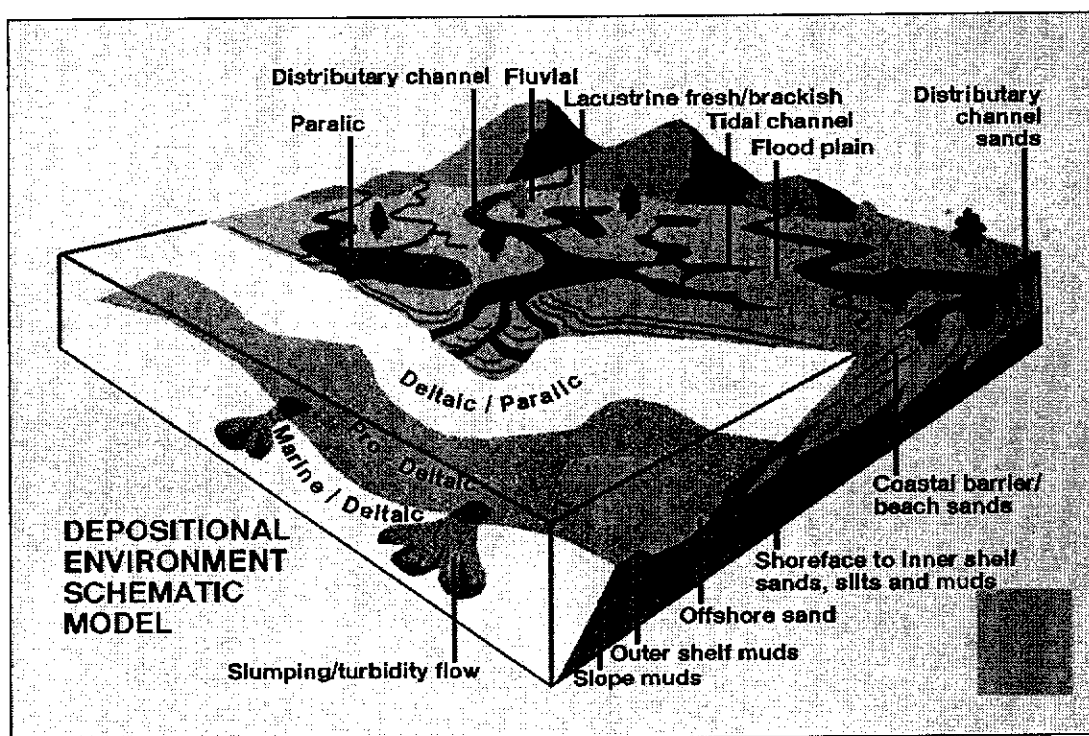
Figure 1.6   Schematic diagram of depositional environments in a delta. Petroleum source rocks can develop in lacustrine, flood-plain, paralic, pro-deltaic and marine deltaic settings. The Eh-pH regime existing during the early diagenesis of organic matter varies accordingly and will affect the kind of lipids preserved. Furthermore, organic matter deposited in a fluvial environment may be eroded, transported offshore and redeposited during periods of sea-level regression.

Research is also needed into the use of land-plant biomarkers as indicators of thermal maturity. Maturity estimation for oils and sediments is routinely accomplished using biomarker compounds derived from bacteria (hopanes) and algae (steranes) (Peters and Moldowan, 1993) but land-plant biomarkers have been used only rarely for this purpose. Noble et al. (1985a) used the ratio of $16\alpha(H)$ and $16\beta(H)$ isomers of phyllocladane as a maturity indicator in the Gippsland Basin while one of the first applications suggested for the oleananes was maturity estimation (Ekweozor and Telnaes, 1990; Ekweozor and Udo, 1988), although they have not subsequently proven popular in this role. As discussed in chapter five, there are special difficulties in using biomarkers to estimate maturity in Tertiary and late Mesozoic deltaic petroleum systems (Grantham, 1986).

1.3   The origin of some land-plant derived biomarkers

Literally hundreds of individual compounds found in oils and sediments have been ascribed an origin from land plants. Indeed, in some oils, the most abundant individual compounds - the n-alkanes - originate primarily from plant-leaf biopolymers and cuticular waxes, either directly or via microbial reworking (de Leeuw and Largeau, 1993 and references therein; Tissot and Welte, 1984). Cyclic biomarkers from land plants are most abundant in deltaic and some lacustrine oils, especially those of late Mesozoic/Tertiary age (Grantham, 1986; Hoffmann et al., 1984; Noble et al., 1991; Robinson, 1987; Williams et al., 1992a,1992b). These include tri- and tetracyclic diterpanes, bicadinanes, oleananes and several unidentified C_{30} compounds (van Aarssen et al., 1990a,1992a; Alam and Pearson, 1990; Robinson, 1987; Woolhouse et al., 1992). Because the biomarker composition of land-plant derived oils is relatively complex, selected ion monitoring GCMS (SIM-GCMS) methods are not always capable of resolving key compounds or of detecting them when present in minor, but nonetheless significant amounts. Higher selectivity methods, such as metastable reaction monitoring GCMS

(MRM-GCMS) provide more information but very few published studies have employed this technique and interpretation is still hampered by the fact that the structures of many compounds are unknown. Furthermore, with the possible exception of oleanane, little is known about the behaviour of higher plant triterpanes during maturation and biodegradation. For example, only two of the numerous isomers and homologs of bicadinane present in Southeast Asian oils have been assigned definitive structures (van Aarssen et al., 1990b; Cox et al., 1986) and little had been published (prior to the present study) on their resistance to thermal stress and biodegradation.

Four classes of plant-derived hydrocarbons are commonly applied in petroleum geochemical studies:

(a)   *n*-Alkanes - especially those associated with plant leaf waxes and/or leaf biopolymers (de Leeuw and Largeau, 1993; Tissot and Welte, 1984)

(b)   Sesquiterpenoid hydrocarbons with the cadinane (Fig. 1.4), murolane, and curcumene skeletons which are found in most land plants (Simoneit et al., 1986 and references therein).

(c)   Triterpenoid hydrocarbons having the oleanane, ursane, lupane, taraxastane and related skeletons (Fig. 1.2) and derived from various functionalised precursors present in the angiosperms (Rullkötter et al., 1994 and references therein). Also fragments of these molecules and skeletally altered triterpenoids such the A-ring contracted oleananes (Smith et al., 1995).

(d)   Resin-derived hydrocarbons - this includes sesqui-, di- and triterpenoid hydrocarbons resulting from thermal dissociation of polymeric plant resins and also the tri- and tetracyclic diterpenoids found in so called leaf resins (Figs. 1.3 and 1.4) which are non-polymeric (Anderson, 1995, Anderson and Crelling, 1995).

1.3.1 Oleananes

The term "oleananes" refers to the sum of 18α-oleanane and oleanane (see Figs. 1.5 and 1.9. They are C_{30} pentacyclic triterpanes found commonly in oils and organic rich sediments of Cretaceous and younger age and less frequently in older sediments (Moldowan et al., 1994). The precursors are considered to be various oxygenated triterpenoids found primarily in the leaves, bark, roots and resins of angiosperms but also in a lichen and some ferns (Ageta and Arai, 1983; Bruun, 1954; Cambie, 1976; Das and Mahato, 1983; Pant and Rastogi, 1979; Whitehead, 1974).

The occurrence of oleananes in the geological record parallels that of the angiosperms (Fig. 1.7). Increases in the frequency of occurrence and abundance relative to other triterpanes are broadly coincident with the main angiosperm radiation in the late Cretaceous and concentrations are highest in samples of Tertiary-age. The oldest sample in which oleananes have been unambiguously identified is a Carboniferous coal ball (Moldowan et al., 1994) but their occurrence in samples older than the Cretaceous is rare.

The most obvious precursors for the oleananes are β-amyrin (olean-12-en-3β-ol) type triterpenoids (Fig. 1.6). However, these are not the only triterpenoids present in angiosperms and compounds with the hopane, ursane, friedelane, taraxastane, multiflorane and lupane skeletons occur with equal frequency (Fig. 1.2; Cambie, 1976; Das and Mahato, 1983; Pant and Rastogi, 1979).
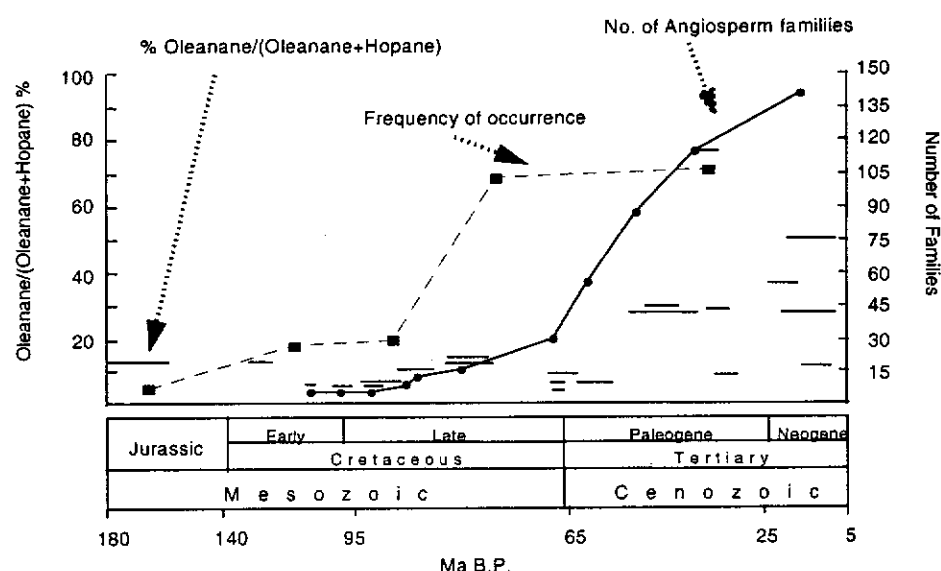
Figure 1.7 Occurrence of oleanane and angiosperm fossils through time (After Moldowan et al., 1994).

Rullkötter et al. (1994) noted that the diversity of triterpenoid skeletons found in living angiosperms was not reflected in a similar diversity among fossil hydrocarbons: oleananes, demethylated lupanes and bicadinanes are the only pentacyclic plant triterpanes reported commonly in geological samples although recent studies (Perkins et al., 1995; Smith, 1995) have suggested that taraxastanes are also widespread. The preponderance of oleananes has been attributed to the tendency of lupene, taraxerene and other unsaturated pentacyclics to undergo acid-catalysed rearrangement, yielding the more thermodynamically stable oleanenes (Fig. 1.8; Rullkötter et al., 1994; ten Haven et al., 1992b; 1992c). The oleanane skeleton can thus be seen as a thermodynamic sink, thereby explaining the abundance of oleananes and the relatively restricted range of other plant triterpanes found in geological samples. Acid conditions also catalyse the conversion of olean-12-ene to a mixture of olean-13(18)-ene, 18α-olean-12-ene and olean-18-ene (Peakman et al., 1991). Oleanane and 18α-oleanane are generated primarily by hydrogenation of the olean-18-ene and 18α-olean-12-ene isomers respectively. The change in the 18α/18β oleanane ratio, which Riva et al. (1988) has shown to be maturity dependant, does not therefore require interconversion of the saturated hydrocarbons. Rather, differential rates of

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destruction/generation are probably responsible for the maturity dependence of the ratio. Furthermore, the α/β ratio would be expected to be sensitive to diagenetic control on the isomeric mix of oleanenes, as well as to maturity. There are indications that this is indeed the case (Smith, 1995).
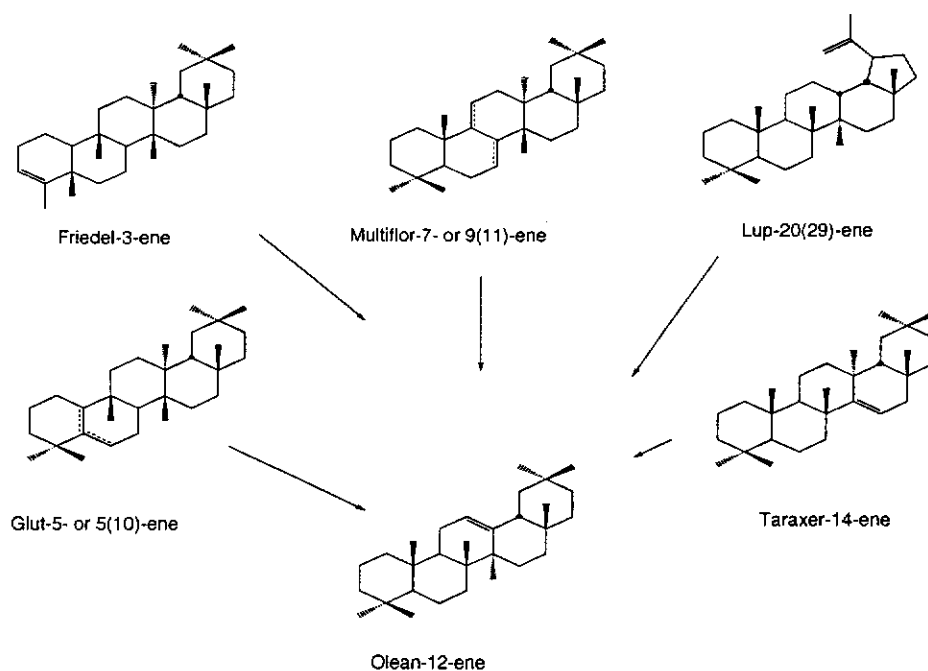
Figure 1.8   Oleanenes can form by acid-catalysed rearrangement of various other plant triterpenoid skeletons (after Rullkötter et al., 1994).

Laboratory experiments and studies of recent sediments or low-maturity geological samples have allowed the fate of plant triterpenoids to be elucidated in some detail. These studies, exemplified by those of Spyckerelle et al. (1977), Chaffee and Johns (1983) on Victorian coals and ten Haven et al. (1992c), Stout (1992) on the Oligocene Brandon lignite, leave little doubt that the main fate of functionalised triterpenoids, at least in terrestrial sediments (coal swamps and lakes), is partial or complete aromatisation. This accords with the comment of Simoneit et al. (1986) that :

"....aromatisation is the main process for the transformation of terrestrial cyclic terpenoids during diagenesis, constituting a general pathway for all terpenoids. "

The presence of extensively aromatised oleanoids, even in recent sediments (La Flamme and Hites, 1979; Jaffe and Elisme, 1995; Wakeham et al., 1980; Wolff et al., 1989) shows that aromatisation is rapid, progressive and almost certainly microbially mediated (Lohmann, 1988). Skeletal alteration involving loss, opening or contraction of ring A and opening or cleavage of ring C occurs in tandem with aromatisation and further depletes the pool of molecules which can end up as oleananes (Stout, 1992 and references cited therein). In view of the importance of aromatisation and rearrangement reactions, it may seem odd that petroleum biomarker studies have made most use of the saturated compounds as indicators of source, depositional environment and maturity. The reason for this is that rearrangement and progressive aromatisation entails loss of the structural features by which the oleanane skeleton is recognised. Furthermore, the mass spectra of the aromatic compounds are less characteristic and so they are less amenable to selective detection by GCMS methods than their saturated counterparts. Consequently, aromatic oleanoids such as 2,9-dimethylpicene (Fig. 1.5) are much less apparent in the aromatic fraction of an oil than are oleananes among the saturated hydrocarbons. Nevertheless, it is important when making use of the saturated compounds to recall that a) they are not the major products of the terrestrial diagenesis of plant terpenoids, and that b) their abundance, relative to other triterpanes, is probably sensitive to early diagenetic conditions.

1.3.2 A-ring contracted oleananes and other rearranged oleananes

Many oils and sediments containing oleananes also contain a series of apparently related compounds (Fig. 1.9). On the basis of their mass spectra and their frequent occurrence with oleanane, these compounds are described hereafter as "oleanoid triterpanes". Their presence has been noted in deltaic oils and sediments from Nigeria, New Zealand, Taiwan, Indonesia and Papua New Guinea (Curiale and Lin, 1991; Ekweozor and Udo, 1988; Murray et al., 1993; Woolhouse et al., 1992). Although some inferences had

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been made about the nature of these compounds from their mass spectra, relative retention times, molecular sieve behaviour and their co-occurrence with oleanane (Armanios et al., 1994; Ekweozor and Udo, 1988; Woolhouse et al., 1992) no definitive structures were established until recently. Consequently they have been given trivial names by various authors (see Table 3.5, chapter three for comparitive terminology). Smith et al. (1995) have now identified some of these compounds as A-ring contracted oleananes - saturated analogs of the A-ring contracted oleanenes identified previously in the Brandon lignite (ten Haven et al. 1992c). The structures of the other compounds remain unknown.
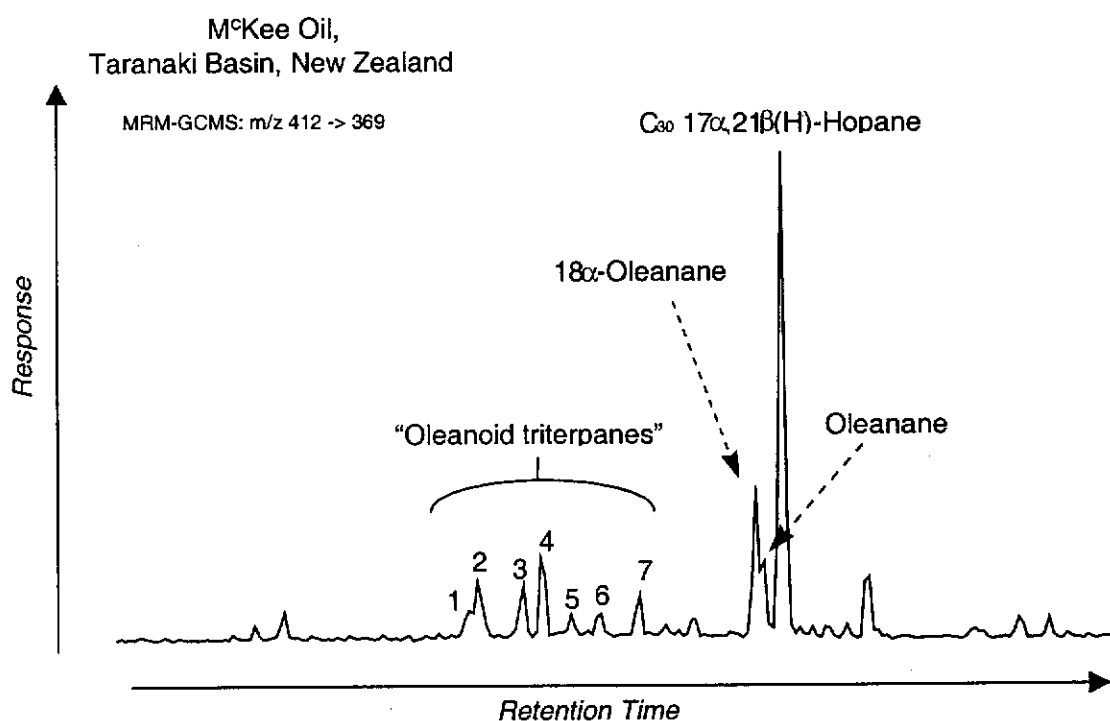
Figure 1.9   Partial MRM-GCMS chromatogram showing the occurrence of oleanoid triterpanes in an oil from New Zealand. Compound 2 has recently been identified by Smith et al. (1995) as an A-ring contracted oleanane (see text). The identities of the other compounds remain unknown.

1.3.3 Plant resins and related sedimentary hydrocarbons

Terpenoid hydrocarbons derived specifically from plant resins have long been known to occur in many crude oils of late Mesozoic and Tertiary-age,

and in some they are major components of the branched/cyclic fraction (van Aarssen et al., 1992a; 1992b; Alexander et al., 1987; Horsfield et al., 1988; Noble et al., 1985a, 1991; Shanmugam, 1985; Snowdon,1991). Fossilised plant resin is known as "amber" or "resinite".

Anderson and Crelling (1995) have defined resinite as:

> " Solid, discrete organic materials found in coals and other sediments as macroscopic or microscopic particles, which are derived from the resins of higher plants "

Plant resins and their fossil analogs (amber or resinite) have attracted man's interest throughout history and have been the subject of detailed archeological, botanical, palaeontological and chemical studies (Gianno, 1990; Langenheim, 1990 and references therein). Recently, there has been renewed interest among geochemists because of the importance of resin-derived compounds as source and age-specific biomarkers in the sedimentary record. Furthermore, although the issue remains controversial, it is possible that resins have an important role in the generation and expulsion of petroleum from terrestrial source rocks (Horsfield et al., 1988; Lewan and Williams, 1987; Mukhopadhyay and Gormly, 1984; Snowdon, 1980, 1991; Snowdon and Powell, 1982). Polycadinene resins (see below) are more thermally labile than other kerogen components (Tegelaar and Noble, 1994) and so, as suggested by Horsfield et al. (1988) may contribute to pore saturation and the formation of a continuous liquid phase in advance of the main stage of kerogen catagenesis. Compounds derived from polycadinene may constitute as much as 10 - 20% of the the mass of a crude oil (van Aarssen et al. 1992a).

Five classes of terpenoid resinites are recognised in the classification scheme developed by Anderson and coworkers (Fig. 1.10). The two types of resinite found most commonly in Ancient sediments contain polymers built from diterpenoid labdatriene and sesquiterpenoid cadinene moeities

respectively. The Class I labdanoid resinites, of which there are three sub-classes, are derived from gymnosperm trees of the families *Araucariaceae*, *Leguminosae*, *Cupressaceae* and *Taxodiaceae*. The Class II sesquiterpenoid resinites arise mainly from angiosperms of the tropical hardwood family, *Dipterocarpaceae* and contain the sesquiterpenoid polymer, polycadinene (Figs. 1.5, 1.10). This polymer has also recently been found in fossil fruits from an unidentified member of the mastixioid *Cornaceae* (van Aarssen et al., 1994). Upon natural or artificial maturation, some Class I resinites yield functionalised labdanoids which serve as precursors for saturate and aromatic bicyclic hydrocarbons in oils (e.g. 1,2,5-trimethylnaphthalene). It should be noted that so-called "resin derived" diterpenoid compounds with the abietane, pimarane, kaurane, phyllocladane and rimuane skeletons (see Alexander et al., 1987; Noble et al., 1985a; Snowdon, 1990) do not appear to be a part of the polymeric structure of resins produced by the *Araucariaceae* and other conifer families (Anderson 1995; K.B. Anderson, pers. comm.). They are however, present in the non-polymeric part of these resins and some compounds may be formed by intra-molecular cyclisation of labdanoid monomers. They are also abundant in the so-called "leaf resins", heartwood and other organs of conifers (Aplin et al., 1963; Cambie, 1976; Cambie et al., 1971). Furthermore, tricyclic resin acids are the major constituent of non-polymeric resins of the *Pinaceae* family (Class V resinites, Fig. 1.10).

Some confusion has arisen over the meaning of the word "dammar". Although linked by historical and commercial association with the resin of dipterocarps, this term is derived from the Malay word for resin and implies no specific botanical origin. In Brunei, for example, the term can also be used to describe the resins of the gymnosperm species *Agathis borneensis* and *Agathis dammara*. Further confusion can arise from the fact that many triterpenoids were first isolated from dipterocarp "dammar" resin and have inherited names such as "dipterocarpol", "dammarol" and "dammarene" (Gupta and Dev, 1971; Mills and Werner, 1955). These triterpenoids were recovered from a solvent extract of the unheated resins and are not related

to the polymeric fraction. In fact, the dammarenes are also present in ferns (Arai et al., 1982) and may also have a microbial origin, since they apparently occur widely in marine sediments (Meunier-Christmann et al., 1991). The Class III (polystyrene) and Class IV (cedrane) resinites are not dealt with in this study as they do not appear to yield hydrocarbons found commonly in petroleum.

The bicadinanes (Fig. 1.4) are C_{30} pentacyclic hydrocarbons formed by dimerisation and reduction of the cadinene units comprising or associated with polycadinene. They were first identified in oils from offshore north Borneo (Grantham et al. 1983) and are widespread in sediments and oils of Tertiary-age from Southeast Asia (van Aarssen et al., 1992a; van Aarssen and de Leeuw, 1989; Alam and Pearson, 1990; Brackman et al., 1984; Curiale et al., 1994; Noble et al., 1991; Stout, 1995). The two main isomers were given the trivial names "W" and "T" before their molecular structures were known but have since been identified as *cis-cis-trans* and *trans-trans-trans* bicadinane respectively (Fig. 1.4; van Aarssen et al., 1990a; Cox et al., 1986). Many other compounds derived from polycadinene have been identified in oils and sediments (van Aarssen et al., 1992a; Sosrowidjojo et al., 1993).

The highest concentrations of bicadinanes occur in Cainozoic-age oils and sediments within the present day realm of the resinous dipterocarps. Reliable dipterocarp fossils date from the early Cainozoic and do not extend beyond the geographic range covered by extant species (Ashton, 1982; Lakhanpal, 1974). Certain genera such as *Hopea* and *Shorea* are prolific resin producers and are the main source of the commercial resin known as dammar (Brackman et al., 1984; Gianno, 1990). Nevertheless, and as predicted by van Aarssen et al. (1994), bicadinanes have now been found in oils and sediments from outside Asia and of pre-Tertiary age, albeit at much lower concentrations (Armanios et al., 1996; Summons et al., 1995).

Class I
Polylabdanoid,
Araucariaceae (esp. Agathis),
Leguminosae, Cupressaceae,
Taxodiaceae, others

Polymer

Polymer

Polymer

Polymer

Polymer

Polymer

Polymer

Polymer

Polymer
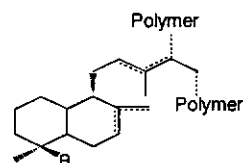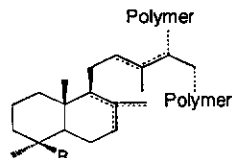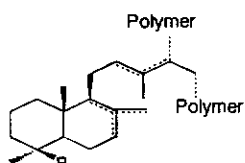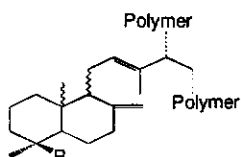
Class Ia:
Including
$R = CO_2H$,
CH_2OH,
O-Succinyl
(?) CH_3
(?) Others

Class Ib:
May include:
$R = CO_2H$,
CH_2OH,
CH_3,
(?) Others
No succinic acid

Class Ic:
May include:
$R = CO_2H$,
CH_3OH,
CH_3,
(?) Others
No succinic acid

Polymer

Class II
Polycadinene,
Dipterocarpaceae,
Cornaceae, (?) Others.

Polymer
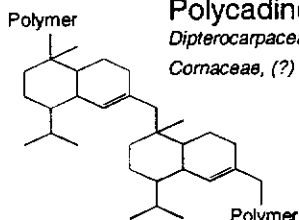
Polymer

Polymer

Class III
Polystyrene,
Hammelidaceae
(esp. Liquidamber)
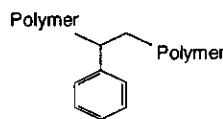
Class IV
Cedrane, sesquiterpenoid,
Non-polymeric
Unknown botanical affinity
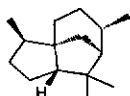
Class V
Abietane/Pimarane,
Diterpenoids,
Labdanoids
normally absent,
Non-polymeric,
Pinaceae

R R'

CO_2H
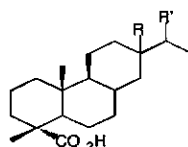
Figure 1.10   The chemical classification system developed by Anderson and co-workers (Anderson and Crelling, 1995; Anderson et al., 1992) for plant resins. Most common botanical affinity also shown (modified from Anderson and Crelling, 1995).

Prior to the present work, the use of bicadinanes as tools for oil-oil and oil-source correlation was very limited and there was no record of their application as maturity or migration markers. This was partly due to the restricted occurrence of these compounds, but also to lack of information

about the factors affecting their abundance, response to thermal maturity and resistance to biodegradation.

However, work carried out by van Aarssen et al. (1992a) suggested that the isomeric distribution of bicadinanes was sensitive to maturity and/or migration and this possibility has been pursued as part of the present project (chapters three and five) and by other workers following the publication of van Aarssen's work (Curiale et al., 1994; Stout, 1995).

1.4   The carbon isotope composition of plant-derived hydrocarbons

The carbon stable isotope composition of a whole petroleum or petroleum sub-fraction has been used as an effective oil-oil and oil-source correlation tool (Peters et al., 1986; Schoell, 1984a, 1984b; Sofer, 1984). However, for reasons set out below, the carbon isotope ratios of whole oils or of fractions based on compound class are less useful than biomarkers in defining source matter type, age and depositional environment. The advent of compound specific isotope analysis (CSIA; Hayes et al., 1990) has allowed a closer assimilation of biomarker and isotope data. Before discussing the significance of this with respect to plant derived hydrocarbons, it is necessary to briefly review the principles of carbon isotope geochemistry.

1.4.1   The origins of carbon isotope discrimination

Eleven out of every thousand carbon dioxide molecules in the atmosphere contain the ^{13}C or "heavy" isotope. Photosynthetic carbon fixation, however, favours the ^{12}C isotope so that organic compounds are isotopically "light" (depleted in ^{13}C) relative to the carbon source. The extent of depletion (or enrichment) is conventionally expressed in the "delta" notation relative to the carbon in the Pee Dee Belemnite (Eqn.1):

$$\delta^{13}C = \frac{\left(\dfrac{^{13}C}{^{12}C}\text{sample} - \dfrac{^{13}C}{^{12}C}\text{standard} \right)}{\dfrac{^{13}C}{^{12}C}\text{standard}} \times 1000 \qquad (1)$$

The units of $\delta^{13}C$ are parts per thousand or per mil (‰) and the terms "heavier" and "lighter" in the context of carbon isotopes refer to relative enrichment or depletion in ^{13}C respectively.

The relationship between the $\delta^{13}C$ of primary photosynthetic carbon ($\delta^{13}C_p$) and that of the carbon source is given by equation 2 (Farquhar et al., 1989):

$$\delta^{13}C_p = \delta^{13}C_{source} + \varepsilon_t + (\varepsilon_f - \varepsilon_t)\frac{P_i}{P_a} \qquad (2)$$

where:

ε_t = fractionation factor for mass transport in air or water = - 4.4‰ (air) or - 0.7‰ (water)

ε_f = fractionation factor at the site of fixation

P_i = Partial pressure of CO_2 at the site of fixation in the cell

P_a = Partial pressure of ambient CO_2 (dissolved or atmospheric)

Algae and land plants having the C3 biosynthetic pathway fix carbon via the Calvin-Benson or RUBISCO cycle for which the effective value of ε_f is ~ - 27‰ (Farquhar et al., 1989; O'Leary, 1988). Atmospheric carbon dioxide, with a present-day $\delta^{13}C$ value ~ - 8‰ (Keeling et al., 1979), is the carbon source for land plants but some marine algae, especially blue-green algae such as Synechococcus, (Popp et al., 1989 and references therein) actively transport and assimilate bicarbonate. This has $\delta^{13}C$ of ~ 0‰, due to the fractionation involved in the hydration of dissolved carbon dioxide. A plot of

Eqn. 2 (Fig. 1.11) shows that the possible range of $\delta^{13}C$ values for primary photosynthate are -12.4 to - 35 ‰ (C3 land plants) and -0.7 to - 27 ‰ (marine algae) depending on P/P_a. The latter in turn depends on the balance between the rates of diffusional supply and photosynthetic consumption of carbon dioxide. Since the diffusion rate is directly proportional to P_a, $\delta^{13}C$ will vary according ambient carbon dioxide pressure and this is the basis of attempts to determine paleo-CO_2 levels through isotope analysis of fossil marine carbon (Myers, 1992; Popp et al., 1989).
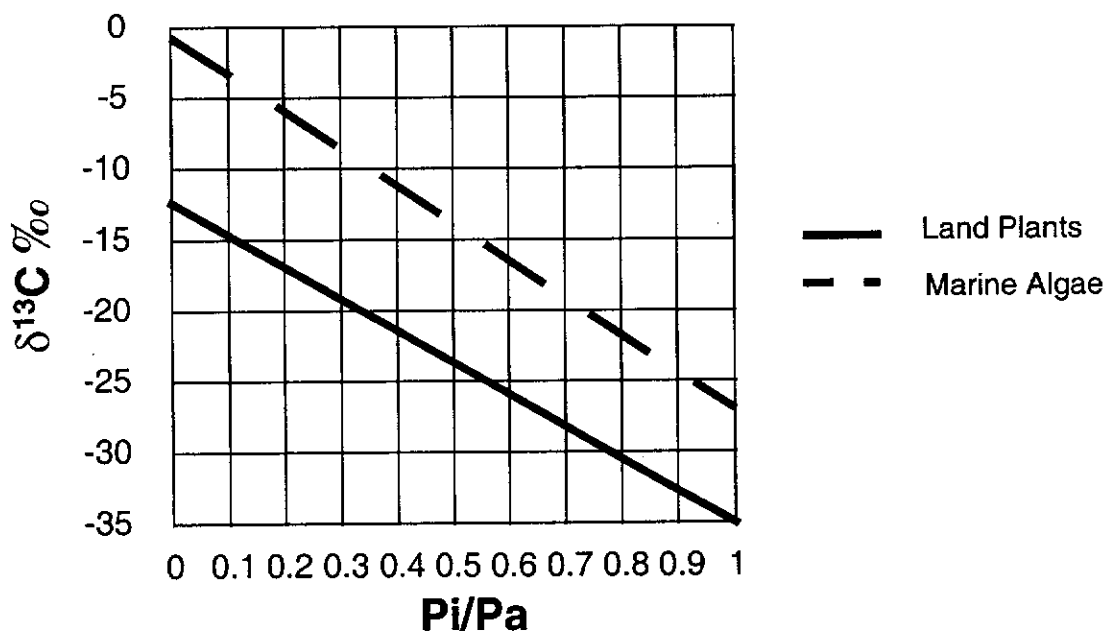
Figure 1.11   Theoretical relationship between the intercellular (Pi) and ambient (Pa) partial pressures of carbon dioxide and the $\delta^{13}C$ ratio of the primary photosynthate. Based on Farquhar et al. (1989).

1.4.2 Factors affecting the carbon isotope ratio of extant and fossil land-plant carbon

The isotope ratio of land-plant carbon has been considered less sensitive than that of marine organic carbon to short-term changes in atmospheric pCO_2 (Popp et al., 1989). This is because a) diffusion of carbon dioxide in air is four orders of magnitude faster than in water so that mass transfer is less likely to be limiting, and b) land plants are partly able to compensate for a

reduction in pCO_2 by increasing stomatal conductance (Farquhar et al., 1989 and references therein). In addition, $\delta^{13}C$ for land plant carbon is not subject to the strong temperature control on the solubility of carbon dioxide in water and so maybe less affected by climatic change and paleolatitude than marine algal carbon. In keeping with these theoretical considerations, Farquhar and others (1982) found that short-term changes in pCO_2 did not affect P_i/P_a for land plants. Nevertheless, many factors can and do affect the degree to which land-plants discriminate against ^{13}C. Some of these are:

1. **Secular change in the atmospheric pressure and/or isotope composition of carbon dioxide**: For example, modern marine organic matter is 5 - 7 ‰ enriched in ^{13}C with respect to that in Cretaceous and older sediments (Arthur et al., 1985; Popp et al, 1989). The change appears to have occurred sometime between the late Eocene and early Miocene (Popp et al., 1989) and has been attributed to a reduction in atmospheric pCO_2 (Arthur et al., 1985). Although it has been suggested that there is no parallel change in $\delta^{13}C$ values for land plant organic matter over this period (Bocherens et al., 1994; Popp et al., 1989 and references therein), very few valid data are available.

2. **Biosynthetic pathways:** Some land plants, such as tropical grasses and many saltmarsh species, fix carbon via the C4 or Hatch-Slack pathway which has a lower fractionation factor than RUBISCO. This results in whole plant $\delta^{13}C$ values of - 12 to -14 ‰ (Farquhar et al., 1989 and references therein). Other plants, mainly desert succulents, use the crassulacean acid metabolism or CAM pathway which gives variable but generally heavier $\delta^{13}C$ values than RUBISCO.

3. **Growth rates:** The fractionation factor has been shown to depend on growth rate for C3 plants (Jansen, 1962; Sheu et al., 1996) as it does for marine algae (Laws et al., 1995) and bacteria (Summons et al., 1994)

4. **Variation among species and in response to short-term environmental change:** The $\delta^{13}C$ values of leaf constituents vary among tree species (Collister et al., 1994; Lloyd and Farquhar, 1994; Lockheart et al., 1997; Saurer et al., 1995), show latitudinal, seasonal and photoperiodic effects (Farquhar et al., 1989; Lockheart et al., 1997; Stuiver and Brazunias, 1987; Vogel, 1993) and vary with altitude in response to reduced pCO_2 (Marshall and Zhang, 1993). The isotope composition of plant carbon is also sensitive to groundwater salinity and to water availability (Farquhar et al., 1989 and references therein; Guy et al., 1986; Longstreth and Noble, 1977; Seeman and Critchley, 1985).

5. **The canopy effect:** Recycling of isotopically light carbon from degrading floor litter occurs in enclosed forests (the "canopy" effect: Broadmeadow and Griffiths, 1993). This means that $\delta^{13}C$ values for the forest as a whole are more negative than for trees growing in relative isolation, e.g. those on the forest margin.

6. **Biochemical fractionation within the plant:** All of the factors listed above affect the isotopic composition of the primary photosynthate. However, further fractionations accompany the synthesis and transport of secondary cellular constituents such as cellulose, lignin and lipids within the plant. Generally, cellulose is enriched in ^{13}C relative to lignin (Benner et al., 1987) which is in turn heavier than the lipids (Schoell, 1984a). Furthermore, Leavitt and Long (1982) showed that cellulose in the leaves of 10 Juniper trees was on average 2 ‰ more depleted in ^{13}C than the same compound in the wood. Theoretical considerations suggest that acetogenic lipids such as the n-alkanoic acids should be ~ 1.5 ‰ more ^{13}C depleted than polyisoprenoidal lipids derived from the same primary carbon (Hayes , 1993; Monson and Hayes, 1982) although Lockheart et al., (1997) have shown that this is not always so for land-plants.

7.   **Leaf morphology:** An important factor determining the carbon isotope composition of land-plants appears to be leaf morphology and structure. All C3 plants adjust stomatal conductance to mimimise loss of water through the stomata while maximising assimilation of carbon dioxide (Farquhar et al., 1989). Conifers, which generally have a narrow leaf morphology, are more water conservative and assimilate carbon less efficiently than broad leaf species, i.e., most angiosperms. Hence, a systematic carbon isotope difference is found between conifer and angiosperm wood (Fig. 1.12: Lloyd and Farquhar, 1994 and references therein; Marshal and Zhang, 1993; Saurer et al., 1995; Stuvier and Braziunas, 1987). Furthermore, a difference may exist between conifers and angiosperms at the level of the forest, as well as for individual trees: Broadmeadow and Griffiths (1993) noted that the canopy effect - the recycling of detrital carbon from the forest floor - was greater for a tropical rain forest in Amazonia than for a temperate Huon pine forest in Tasmania. Interestingly, no significant difference in the magnitude of the canopy effect for tropical as opposed to temperate forests was observed where both were dominated by broad-leaf angiosperms.

The factors listed above cause relatively short-term and in most cases local variation in the carbon isotope composition of land-plant carbon. However, fundamental differences, such as in the way conifers and angiosperms assimilate carbon, could overwhelm the averaging effects of space and time and leave their mark in the geological record. In fact, two of the most significant ecological events in the southern hemisphere were the late Triassic emergence of the Araucarian conifer flora and it's subsequent displacement by the angiosperms during the late Mesozoic - Tertiary (Alexander et al., 1992). As will be shown, the latter event appears to be reflected in differences between the carbon isotope composition of otherwise similar oils from Australia and New Zealand.

Generally speaking, petroleum is considered to be derived mainly from plant and bacterial lipids (Tissot and Welte, 1984) and especially the leaf lipids in the case of land-plant derived oils (Killops et al., 1995 ; de Leeuw and Largeau, 1993). Although this view has been questioned on the basis of deuterium isotope measurements (Schoell, 1984a) an origin from the relatively isotopically light lipids seems necessary to explain crude oils being invariably depleted in ^{13}C with respect to the bulk organic carbon in the source (Peters and Moldowan, 1993 and references therein).

Average 3 ‰ difference in $\delta^{13}C$

Conifer Forest	Angiosperm Forest
Narrow leaf morphology	Broad leaf morphology
Water conservative	Less water conservative
Restricted access to CO_2	Less restricted access to CO_2
Discriminates less against ^{13}C	Discriminates more against ^{13}C
Open canopy structure	Closed canopy structure
Less recycled CO_2	More recycled CO_2
$\delta^{13}C$ values for **wood** typically*	$\delta^{13}C$ values for **wood** typically*:
~ - 21‰	~ - 24‰

Figure 1.12   Conifers (gymnosperms) differ fundamentally from broad-leaf angiosperms in the extent to which they discriminate against ^{13}C. *Data from Stuiver and Braziunas (1987) for modern plants growing at 40° latitude.

This is especially so when it is recalled that bacterial reworking of the primary organic matter during early diagenesis causes an increase in $\delta^{13}C$ values of about 1-2 ‰ (Coffin et al., 1990; De Niro and Epstein, 1978)

1.4.3 The carbon isotope composition of n-alkanes

Because of the many factors which can affect the isotope ratio of plant carbon, interpreting the $\delta^{13}C$ of oils in terms of source matter type and paleoenvironment is very difficult. However, useful information may be obtained where independent control on source character is available. Hence, Peters et al. (1986) successfully distinguished marine and non-marine oils using a combination of biomarker and isotope data, whereas reliance on carbon isotope values alone failed in one third of cases. In that study, biomarker and isotope data were employed as independant but complementary parameters. However, an even more effective integration of biomarker and isotope data can be achieved via determination of the isotope composition of individual biomarkers.

Rapid compound specific isotope analysis or CSIA has become possible with the successful combination of a gas chromatograph and isotope ratio mass spectrometer via a combustion interface (GC-IRMS; Hayes et al. 1990). Using this technique, Freeman and co-workers (1989) have shown that there is great variability in the isotope composition of sedimentary lipids and it has been suggested (Bjorøy et al., 1991; Gilmour et al., 1984; Rieley et al., 1991) that compound specific isotope data could improve the reliability of source characterisation for oils. Given that individual n-alkanes arise from diverse precursors (Tissot and Welte, 1984 and references therein) and that these precursors may be isotopically distinct (Collister et al., 1992, 1994; Schoell, 1984b), variation in source character should appear as change in the shape of the n-alkane isotope profile - that is, in the shape of a plot of carbon number vs. $\delta^{13}C$ for the n-alkanes. Collister et al. (1992) and Boreham et al. (1994) made effective use of this fact in their studies of the origin of n-alkanes in oil shales and thereby provided much of the framework for interpreting n-alkane isotope profiles in oils. However, a stronger theoretical framework and a larger empirical database are needed to support routine use of the technique in oil-oil and oil-source rock correlation. Knowledge of the isotope composition of individual n-alkanes also enables prediction of

how the $\delta^{13}C$ value of a whole oil or sediment will change in response to maturation, evaporative fractionation (Dzhou and Hughes, 1993) and various degrees of biodegradation. Such knowledge can be very useful in oil-oil correlation.

1.4.4 The carbon isotope composition of resins and resin-derived compounds

As discussed earlier, resin-derived hydrocarbons are important constituents of many terrigenous oils. Despite this, very little is known about the carbon isotope composition of plant resins and their fossil counterparts (resinites). Because of the importance of carbon isotope technology in the field of plant physiology and ecology, there is a wealth of published data on the carbon isotope composition of leaves, wood, flowers and other plant tissues (see Bocherens et al., 1994 for a review of fossil plant data). However, a search of both the botanical and geological literature prior to this project revealed only two references to the carbon isotope composition of resins or resinite. Smith et al. (1982) reported $\delta^{13}C$ values for resinite and other macerals in some Australian coals while Horsfield et al. (1988) correlated the resin content of some Indonesian oil-prone coals with their carbon isotope ratios. In view of the paucity of resin isotope data, an aim of the present project was to measure $\delta^{13}C$ for a range of resin and resinite samples and so develop a better understanding of how resins and the hydrocarbons derived from them influence the isotopic composition of oils.

1.5   Aims, scope and significance of this work

The aim of this project is to gain a better understanding of the factors controlling the occurrence, relative abundance and carbon isotope composition of land-plant derived compounds in crude oils and Ancient sediments. It is hoped that this will assist oil-oil and oil-source correlation as

well as providing insight into the conditions needed for the development of oil-prone source rocks. A subsidiary theme is the effective combination of biomarker and *n*-alkane isotope data to define source type, depositional environment and maturity, especially for land-plant derived oils of late Mesozoic to Tertiary age.

CHAPTER 2:   EXPERIMENTAL

2.1   Samples

Samples for this study were crude oils, Ancient sediments, fresh tree resins and fossil resins (resinites).

2.1.1 Oils

Crude oils used for this study were selected from the collection of the Australian Geological Survey Organisation (AGSO) with an emphasis on oils containing compounds of angiosperm origin. Details of the origin of the oil samples and references to the age and character of the source rocks (where known) are given in Table 2.1. The terms FD, LAC etc. are descriptive of the known (or in some cased inferred) depositional environment of the source rocks - see chapter three. Not all the oils listed in Table 2.1 were available throughout the study so different subsets were used for the work described in chapters three and five. All except FD SSB 1 - 3, FD B 1, FD B2 , FD P and FD G were included in the work for chapter three and all those marked with an asterisk in the work for chapter five.

2.1.2 Sediments

Sediment samples were obtained from outcrop section or from exploration (coal or petroleum) wells in the Buller Basin (New Zealand), Southeast Luzon and Visayan Basins (Philippines) and South Sumatra Basin (Indonesia). A single sample from the Gippsland Basin (Australia; courtesy of Dr. C. Boreham) was used in the study of carbon isotopes of resin compounds

(chapter four) but was not otherwise analysed. Descriptions of the location, age, environment and lithology of the samples are given in Table 2.2 along with basic geochemical data.

Sediments from the Visayan Basin, the Philippines were collected during a survey by Australian Worldwide Exploration (oil samples TR1 and TR2, Table 2.1, were collected during the same survey). The samples are from outcrop section in the Miocene Taog, Tagnocot and Bata formations exposed on the Island of Leyte. The kerogens are of mixed lacustrine algal and land plant origin and are immature to early oil-window maturity (Murray et al., 1992; Wehner, 1989).

Samples from the South Sumatra Basin are cuttings from the GK well (South Palembang sub-basin) and were provided by Pertamina (Indonesia), through Dr. I.B. Sosrowidjojo. The geology and tectonic evolution of the area have been described in detail elsewhere (Adiwidjaja and de Coster, 1973; Pulunggono et al., 1992), but for convenience a generalised stratigraphy is shown in Fig. 2.1. The basin is a half-graben structure formed during east-west extension during the late Mesozoic and early Tertiary periods. The pre-Tertiary basement is overlain unconformably by volcanoclastic rocks with intermittent lacustrine shales (Lahat Formation) followed by the deltaic to shallow marine Talang Akar formation. The coals and carbonaceous shales of the Talang Akar formation are the primary source of oil and gas in the South Sumatra Basin as they are in the Ardjuna Basin of Northwest Java (Noble et al., 1991; Rudyanto et al., 1994). However, lacustrine shales of the Lahat formation, analogous to the prolific algal shales of the Central Sumatra Basin also contribute to oil generation in some areas (Rudyanto et al., 1994; Suseno et al., 1992). The Talang Akar formation is overlain by the marine shales of the Gumai Formation which contain appreciable quantities of immature, oil-prone organic matter. The samples used for this study are from a section through the Gumai and Talang Akar formations where the depositional environment changes from marine, through shallow marine/paralic to fluvio-deltaic with increasing depth. Consequently, the

shallower samples contain a mixture of marine and terrestrial organic matter, while most of the deeper samples contain predominantly bacterially reworked higher-plant matter. Only the deepest samples have entered the oil window and the zone of peak oil generation is not penetrated by the GK well. However, other wells in the basin have penetrated this zone (Sosrowidjojo et al., 1994). Basin modelling (Sosrowidjojo et al., 1994) suggests an increase in heat flow approximately 4 Ma b.p. so that the shallower sediments may have experienced slightly more rapid heating than those at depth. Nevertheless, the burial and thermal history remains relatively simple and for the purposes of this study increasing depth is equated to an increasing time-temperature integral.

Age Ma	EPOCH		STRATIGRAPHIC UNIT
2	Pliocene		Kasai Fm
6-7			?
12	Late	Miocene	Muara Enim Fm
16	Middle	Miocene	Air Benakat Fm
	Early	Miocene	Gumai Fm
23.5			Batu Raja Lst / Talang Akar Fm
30	Oligocene		
37.5	Eocene		Lahat Fm ?
57			
65	Paleocene		
	Pre-Tertiary		
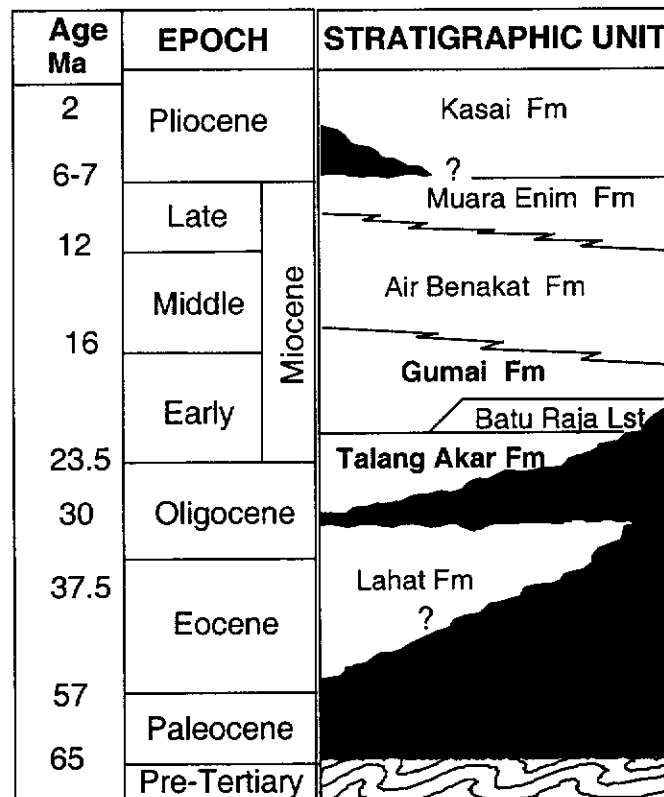
Figure 2.1   Generalised stratigraphy of the South Sumatra Basin (after de Coster, 1974; Hasan and Soebandrio,1988).

Sediments from the Buller coalfield (New Zealand) are composite core sections from Coal Research Limited (NZ) drillhole 1281/1494 in the upper

Waimangaroa Sector of the Brunner Coal measures. The samples, which are of Eocene age, are referred to hereafter as the "Buller coals". Further description can be found in chapter six, Norgate (1995) and Newman (1991). The samples were provided by Dr. Jane Newman of Coal Research Ltd. (NZ) and the University of Canterbury.

A single core of marginally mature Miocene-age coal was obtained from the Maniguin-2 well, Maniguin Island, the Philippines. This sample, referred to hereafter as the "Maniguin coal" , was provided by Dragon Oil Ltd.
Further details of the stratigraphy, depositional setting and palynology of the Maniguin coal, Buller coals and South Sumatra Basin sediments are given in chapters five and six.

2.1.3 Resins and resinites

Freshly bled trunk resins were collected from trees in the Sydney Botanic Gardens, Wollemi National Park (courtesy of Dr. K. Hill), Brighton Le Sands near Sydney (courtesy of R. Summons), Manutuke and Makaretu Stm., New Zealand (courtesy of D. Francis), Belalong forest research station, Temburong, Brunei Darussalam (courtesy of W. Booth, Universiti Brunei Darussalam) and Mt. Stromlo forest reserve, Canberra.

Fossil resin samples were obtained from the Yallourn open-cut coal mine, Victoria (courtesy of Dr. C. Boreham), Westport and Greymouth coal fields, New Zealand (courtesy of Dr. J. Newman), Blind Canyon Mine, Utah, USA (courtesy of Dr. A. Davis), outcrop coals on Jalan Sungei Akar, Bandar Seri Begawan, Brunei Darussalam (courtesy of Dr. W. Booth) and as jetsam on the Southern Australian coast (Murray et al., 1994).

Table 2.1   Details of crude oil samples.

Fluvio-Deltaic (FD)

Number/Label	AGSO #	Name	Basin	Region/Country	Age of Source	References/Notes
FD 1*	772*	Conf.	Tarakan	Borneo, Indonesia	Miocene ?	Samuel, 1980
FD 2*	773*	Conf.	Tarakan	Borneo, Indonesia	Miocene ?	Samuel, 1980
FD 3*	537*	Conf.	Ardjuna	Indonesia	Oligocene	Noble et al.; 1991; Rudiyanto et al., 1994
FD 4*	733*	McKee	Taranaki	New Zealand	Eocene	Czochanska et al., 1988; Killops et al., 1994b
FD 5	731	Maui-1	Taranaki	New Zealand	L. Cretaceous	Czochanska et al., 1988; Killops et al., 1994b
FD 6*	372*	Conf.	Ardjuna	Indonesia	L. Oligocene	Noble et al.; 1991
FD 7	728	Conf.	Ardjuna	Indonesia	L. Oligocene	Noble et al.; 1991
FD 8	701	MST-11	Visayan	Cebu, Philippines	L.Cretaceous?	Wehner, 1989
FD 9*	540*	Conf.	South Sumatra	Indonesia	Oligocene	Williams et al., 1992a; Rudiyanto et al., 1994
FD 10*	791*	BS-OS-01	SE Luzon	Bondoc, Philippines	Miocene ?	Lee et al., 1994
FD 11*	735*	Reina Regente	Visayan	Cebu, Philippines	L.Cretaceous?	Wehner, 1989; AGSO unpublished
FD 12*	542*	Conf.	South Sumatra	Indonesia	Oligocene	Williams et al., 1992a; Rudiyanto et al., 1994
FD 13*	743*	Lufa Seep	Papuan	P.N.Guinea	Tertiary	Murray et al.; 1993
FD SSB1*	-	Conf.	South Sumatra	Indonesia	Oligocene	
FD SSB2*	-	Conf.	South Sumatra	Indonesia	Oligocene	
FD SSB3*	-	Conf.	South Sumatra	Indonesia	Oligocene	
FD B1*	10026	Iron Duke	Offshore Brunei	Brunei	Miocene	Ellenor (1984)
FD B2*	10029	Kekidi	Offshore Brunei	Brunei	Miocene	Ellenor (1984)
FD P*	404	Gingin	Perth	Australia	Jurassic ?	Summons et al. (1995)
FD G	10032	Dolphin	Gippsland	Australia	L. Cretaceous-Tertiary	Biodegraded (light)
FD H	10031	Halibut	Gippsland	Australia	L. Cretaceous-Tertiary	
FD C	145	Basker	Gippsland	Australia	L. Cretaceous-Tertiary	

Table 2.1 (cont.)

Number/Label	AGSO #	Name	Basin	Region/Country	Age of Source	References/Notes
Transitional (TR)						
TR 1	698	Leyte Seep	Visayan	Leyte, Philippines	Miocene	Wehner, 1989 and AGSO unpublished
TR 2	689	Leyte Seep	Visayan	Leyte, Philippines	Miocene	Wehner, 1989 and AGSO unpublished
TR 3	322	Conf.	Pearl River Mouth	Hainan, S.China	Eocene	P. Price, pers. comm.
Lacustrine (LAC)						
LAC 1	436	Minas	Central Sumatra	Indonesia	Eocene-Oligocene	Williams et al., 1985; Seifert and Moldowan, 1981.
LAC 2	435	SE Balam	Central Sumatra	Indonesia	Eocene-Oligocene	Williams et al., 1985; Seifert and Moldowan, 1981.
LAC 3	437	Duri	Central Sumatra	Indonesia	Eocene-Oligocene	Williams et al., 1985; Seifert and Moldowan, 1981.
Saline Lacustrine (SAL)						
SAL 1	350	Bluebell	Uinta	Utah, U.S.A.	Eocene	Seifert, 1978
SAL 2	345	Redwash	Uinta	Utah, U.S.A	Eocene	Seifert, 1978
SAL 3	803	Xiang-10	Dongting	China	E. Tertiary/L.Cretaceous ?	Williams et al., 1992a
Marine Deltaic (MD)						
MD 1	873	Conf.	N.Palawan	Philippines	E. Tertiary/L.Cretaceous ?	AGSO unpublished, H.H.Williams, Pers. Comm.
MD 2	748	Waitangi Seep	East Coast	New Zealand	Late Cretaceous?	Murray et al., 1994b; Johnston et al., 1992
MD 3	535	Kora	Taranaki	New Zealand	Paleocene	Reed, 1992; Murray et al., 1994b; Killops et al., 1994b
Marine Carbonate (MC)						
MC 1	739	Linapacan-1	N.Palawan	Philippines	E. Tertiary/L.Cretaceous ?	Williams et al., 1992b
MC 2	787	Nido-1	N.Palawan	Philippines	E. Tertiary/L.Cretaceous ?	Williams et al., 1992b

Table 2.1 (cont.)

Number/Label	AGSO #	Name	Basin	Region/Country	Age of Source	References/Notes
MC 3*	738	Galoc-2	N.Palawan	Philippines	E. Tertiary/L.Cretaceous ?	Williams et al., 1992b
MC 4	740	Octon-1	N.Palawan	Philippines	E. Tertiary/L.Cretaceous ?	Williams et al., 1992b

Conf. = Confidential.

* denotes oils used for the study of bicadinane maturity indicators (chapter five).

Table 2.2   Details of sediment samples

Philippines, Visayan Basin sediments, Outcrop

Depth (m)	Formation	Age	Environment	Lithology	Ro (%)†	TOC (Wt. %)	EOM/ TOC‡	Rock Eval Tmax °C	Rock Eval HI§	Rock Eval PI§
Surface 1	Taog	Miocene	Floodplain/Lacustrine	Shale		20.2	0.07	438	196	0.09
Surface 2	Taog	Miocene	Floodplain/Lacustrine	Shale		1.13	0.16	446	109	0.27
Surface 3	Taog	Miocene	Floodplain/Lacustrine	Shale		2.92	0.09	431	71	0.05
Surface 4	Taog	Miocene	Floodplain/Lacustrine	Sltstn/Sndstn		3.23	0.10	438	169	0.01
Surface 5	Taog	Miocene	Floodplain/Lacustrine	Shale		1.70	0.06	435	698	0.01
Surface 6	Taog	Miocene	Floodplain/Lacustrine	Shale		3.42	0.09	439	484	0.02
Surface 7	Taog	Miocene	Floodplain/Lacustrine	Shale		3.47	0.10	437	245	0.06
Surface 8	Taog	Miocene	Floodplain/Lacustrine	Shale		2.26	0.10	437	348	0.05
Surface 9	Taog	Miocene	Floodplain/Lacustrine	Shale	0.46	2.89	0.12	440	425	0.07
Surface 10	Taog	Miocene	Floodplain/Lacustrine	Shale		3.38	0.08	439	224	0.03
Surface 11	Taog	Miocene	Floodplain/Lacustrine	Shale		3.16	0.04	438	211	0.05
Surface 12	Taog	Miocene	Floodplain/Lacustrine	Shale		1.64	0.07	452	81	0.13
Surface 13	Taog	Miocene	Floodplain/Lacustrine	Shale		3.57	0.07	439	642	0.04
Surface 14	Bata	Miocene	Floodplain/Lacustrine	Sltstn		0.78	0.05	427	84	0.09
Surface 15	Bata	Miocene	Floodplain/Lacustrine	Shale		1.27	0.24	433	142	0.13
Surface 16	Tagnocot	Miocene	Floodplain/Lacustrine	Shale		2.73	0.05	435	623	0.04

Table 2.2 (cont.) Details of sediment samples.

Depth (m)	Formation	Age	Environment	Lithology	Ro (%)[†]	TOC (Wt. %)	EOM/TOC[‡]	Rock Eval		
								Tmax °C	HI[§]	PI[¶]
New Zealand, Buller Basin, Drillhole 1281/1494 [ξ]										
255.6 - 255.9'	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.56	77	0.15	432	316	0.07
255.9 - 256.5	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.57	75	0.14	429	314	0.07
257.1 - 258.2	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.62	77	0.13	430	287	0.07
258.2 - 259.4	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.67	78	0.11	437	275	0.06
261.3 - 262.4	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.71	78	0.10	435	257	0.05
262.4 - 263.0	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.71	78	0.09	436	268	0.05
264.0 - 264.7	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.72	78	0.09	436	287	0.04
264.7 - 265.4	Buller Coals	Eocene	Fluvio-Deltaic	Coal	0.71	76	0.09	440	265	0.05
Philippines, Maniguin Island, Maniguin-1 well										
2268	Maniguin Coal	Miocene	Floodplain/Lacustrine	Coal	0.66	66	0.06	421	277	0.06
Indonesia, South Sumatra Basin, GK well										
1114	Gumai	Miocene	Marine	Shale	na	0.96	0.21	437	77	0.10
1270	Gumai	Miocene	Marine	Shale	0.4	0.94	0.14	430	133	0.20
1351	Gumai	Miocene	Marine	Shale	0.5	0.60	0.28	430	202	0.20
1463	Talang Akar (TRM)	Miocene	Shallow marine	Shale	0.6	1.5	0.15	435	245	0.18
1514	Talang Akar (TRM)	Miocene	Shallow marine	Shale	na	0.96	0.20	431	217	0.14
1742	Talang Akar (TRM)	Miocene	Fluvio-Deltaic	Coal	0.6	53	0.12	431	411	0.07
1802	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Shale	0.6	1.60	0.16	437	146	0.20

Table 2.2 (cont.) Details of sediment samples.

Depth (m)	Formation	Age	Environment	Lithology	Ro (%)†	TOC (Wt. %)	EOM/TOC‡	Rock Eval		
								Tmax °C	HI§	PI§
1862	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Coal	na	64	0.11	436	408	0.11
1959	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Coal	na	64	0.10	437	402	0.10
2026	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Coal	0.7	64	0.12	440	353	0.11
2069	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Carb. Shale	na	3.6	0.11	440	346	0.11
2259	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Coal	0.9	43	0.09	445	315	0.10
2309	Talang Akar (GRM)	Oligocene	Fluvio-Deltaic	Coal	0.9	43	0.07	446	325	0.09

Australia, Gippsland Basin, Tuna #2 well

| 2030 | - | Eocene | Deltaic | Shale | - | 46 | - | 426 | 359 | 0.05 |

TRM = Transitional member, GRM = Gritsand member, † Mean vitrinite reflectance ± 0.1% RSD for GK samples, ± 0.05% others. 19 to 42 phytoclasts measured. ‡ Weight fraction of extractable organic matter per unit TOC. § Rock Eval: HI = kg hydrocarbon (S2)/tonne⁻¹ TOC. PI = S1/(S1+S2) ʄ Data from Norgate (1995), ʡ Composite samples
na: not available

Further details of the origin, age (where known) and botanical affinity of the resin and resinite samples are given in chapter four (Tables 4.1 and 4.2). Samples were ground in a mortar and pestle before analysis and no attempt was made to separate polymeric and non-polymeric components.

2.2 Analytical methods

2.2.1 Rock Eval/TOC of sediments

Rock Eval pyrolysis of sediment samples (10 - 50 mg) was carried out on a Girdel Rock Eval instrument and Total Organic Carbon (TOC) on a Leco instrument in both cases using the standard conditions specified by the manufacturers.

Briefly, TOC determination required the sample to be ground to less than 63 μm in size, and digested in a 50 fold volume of 5M HCl at room temperature over 18 h to remove carbon associated with mineral carbonates. The residue was filtered and washed with distilled water until neutral in a LECO filtering crucible. The crucible containing the sample was then dried at 50°C and elemental copper and iron accelerators added to assist the combustion of the sample. It was then introduced to a LECO induction furnace coupled to a LECO Carbon Determinator model DC12 for analysis. The instrumental process involved the burning of the sample in a stream of oxygen in the induction furnace, all carbon being oxidised to CO_2 and CO. The CO was converted to CO_2 via catalysis, contaminant gases removed, and the CO_2 trapped on a molecular sieve. The CO_2 was released by heating to a TCD detector and the concentration determined by reference to a potassium hydrogen phthalate standard treated in the same way.

A description of the theory and operation of "Rock Eval" can be found in Tissot and Welte (1984). The sample to be analysed was ground to particles less than 63 μm in size then weighed into crucibles and analysed on a Rock

Eval II to produce Tmax (°C), S1, S2 and S3 values, under the following conditions: CYCLE 4, initial 300 °C isothermal for 5 min., 25 °C/min. temperature gradient to 550 °C, a final isothermal hold at 550 °C for 1 min. and CO trap shut off at 390 °C. S1 and S2 units are mg hydrocarbons/g of rock. S3 units are mg CO_2/g of rock. PI and HI are values calculated as follows: PI (Production Index) = S1/(S1+S2). HI (Hydrogen Index) = 100*S2/TOC (Total Organic Carbon). T_{max} is the temperature at which the maximum rate of hydrocarbon evolution occurs (peak S2).

2.2.2 Preparation of sediment extracts

Core fragments, outcrop samples and washed cuttings (1 - 20 g) were dried at 60 °C overnight and then crushed in a ring-mill to pass a 200 mesh screen. After sub-sampling for Rock Eval pyrolysis and Total Organic Carbon (TOC) determination, the powdered sediment was either a) extracted in a soxhlet apparatus for 48 h with redistilled chloroform:methanol (87:13) or b) extracted with an azeotropic mixture of dichloromethane and methanol (50 ml) for 2-3 h in an ultrasonic bath. The extract was filtered (0.2 µM) and rotary evaporated to near dryness. It was then transferred to a 4 mL vial and blown under a gentle stream of nitrogen to remove the remaining solvent and permit gravimetric determination of total extractable organic matter (EOM). Elemental sulphur was removed by passing the extract, redissolved in pentane, through a column (5 g) of activated copper powder.

2.2.3 Asphaltene removal and column chromatograpy

Asphaltenes were precipitated from sediment extracts and oils by dilution of a dichloromethane solution with a 50-fold excess of pentane. The asphaltene free samples were then were separated into aliphatic, aromatic and polar fractions by chromatography on silica gel (12g, activated, 200 °C). Saturate hydrocarbons (alkanes and alkenes) were eluted with 40 mL petroleum spirit,

aromatics with 50 mL dichloromethane:petroleum spirit (50:50) and polars with 40 mL dichloromethane:methanol (50:50).

2.2.4 Preparation of n-alkane and branched/cyclic fractions

A portion of the saturate hydrocarbon fraction was applied to the top of a small column (ca. 2g) of Silicalite molecular sieve (Union Carbide) in a pasteur pipette. After allowing the solvent to evaporate, the non-adducted branched/cyclic fraction (Silicalite Non-adduct or "SNA") was recovered by elution of the column with 3 x 5 mL n-pentane. The adducted n-alkanes (Silicalite Adduct or "SA") were recovered by destroying the Silicalite matrix with hydrofluoric acid and partitioning the liberated hydrocarbons into n-pentane.

2.2.5 Gas chromatography

Saturated hydrocarbon fractions were analysed by gas chromatography (GC) on a 25 m x 0.2 mm ID or 50 m x 0.2 mm ID HP Ultra 1 fused silica capillary column (methylsilicone) using on-column injection and a temperature program of 50 to 300 °C at 4 °C min^{-1}. The carrier gas was H_2 at 30 cm sec^{-1}. An internal standard (10 μg 3-methylheneicosane, Chiron) was added prior to analysis.

2.2.6 Gas chromatography-mass spectrometry

Gas chromatography-mass spectrometry (GCMS) analyses were carried out on either a VG 70E/HP 5890 or VG Autospec Ultima Q/Carlo Erba instrument in the full scan, selected ion monitoring (SIM) or linked scan metastable reaction monitoring (MRM) modes. Some SIM-GCMS analyses were also carried out a HP5970 series quadrupole Mass Selective Detector

(MSD) coupled to a HP 5890 gas chromatograph. Saturate hydrocarbon fractions were analysed on 60 m x 0.25 mm ID DB-1 (J&W) or 50 m x 0.32 mm ID HP Ultra-1 column, aromatic fractions on a 25 or 50 m x 0.25 mm ID DB-5 (J&W) column. The carrier gas was H_2 at 30 cm sec^{-1}.

Analyses for diaromatic tricadinanes (chapter five) were performed on either a 30 m x 0.28 mm ID MXT-1 Restek stainless steel column or a 15 m x 0.18 m ID DB-5 (J&W) column. In the former case, the final column temperature was held at 360 °C for 50 minutes to achieve elution of the C_{45} compounds.

For SIM-GCMS and MRM-GCMS analyses, internal standards of trideuterated (D3) CD_3-cholestane and/or tetradeuterated (D4) $5\alpha,14\alpha,17\alpha$ 20S-Stigmastane (Chiron) were added to the samples prior to analysis (100 ng added per 1 mg of saturates or branched/cyclic fraction). The ions monitored in SIM- and MRM-GCMS and the principal compound classes corresponding to each are shown in Tables 2.3 and 2. 4. These are general purpose acquisition parameters and not all the data generated was used in the current project.

2.2.7 Carbon isotope analysis

The $^{13}C/^{12}C$ ratio was determined on the total organic carbon or bulk saturate fraction for selected samples. Typically 2 mg was sealed in a Vycor tube and oxidised over CuO at 950 °C. The liberated CO_2 was analysed using a VG Sira-12 or Finnigan MAT 252 isotope ratio mass spectrometer.

Table 2.3   Acquisition parameters for SIM-GCMS analyses

Channel	m/z	Ch Time (ms)	I/ch Time (ms)	Compound Class
1	414.4230	40	180	C_{30} Steranes
2	412.4060	40	30	C_{30} Triterpanes
3	400.4070	40	30	C_{29} Steranes
4	398.3900	40	30	C_{29} Triterpanes
5	383.3676	40	30	C_{31} Bicadinanes
6	369.3520	40	30	C_{30} Bicadinanes
7	274.2652	40	50	Tetracyclic diterpanes
8	234.2100	40	70	D3-Methylcholestane standard
9	231.2121	40	30	Ring A-Methylsteranes
10	221.2210	40	45	D4-stigmastane standard
11	218.2030	40	40	Steranes
12	217.1960	40	30	Steranes
13	205.1940	40	40	Ring A-Methylhopanes
14	191.1790	40	50	Triterpanes
15	123.1170	40	170	Diterpanes

Table 2.4   Acquisition parameters for MRM-GCMS analyses

Channel	Parent Ion (m/z)	Daughter Ion (m/z)	Ch Time (ms)	I/ch Time (ms)	Compound Class
1	426.4210	383.3676	40	80	C_{31} Bicadinanes
2	412.4060	369.3520	40	50	C_{30} Bicadinanes
3	389.4105	234.2320	40	200	D3-Methylcholestane standard
4	414.4230	231.2120	40	60	Ring A-Methylsteranes
5	372.3760	217.1960	40	50	C_{27} Steranes
6	386.3910	217.1960	40	50	C_{28} Steranes
7	404.4321	221.2210	40	50	D4-Stigmastane standard
8	400.4070	217.1960	40	50	C_{29} Steranes
9	414.4230	217.1960	40	50	C_{30} Steranes
10	426.4210	205.1940	40	50	C_{31} Ring A-Methylhopanes
11	370.3590	191.1790	40	40	C_{27} Triterpanes
12	384.3740	191.1790	40	50	C_{28} Triterpanes
13	398.3900	191.1790	40	50	C_{29} Triterpanes
14	412.4060	191.1790	40	50	C_{30} Triterpanes
15	426.4210	191.1790	40	50	C_{31} Triterpanes
16	398.3900	177.1640	40	50	C_{29}- 25-Norhopanes
17	468.4670	191.1790	40	50	C_{34} Triterpanes
18	412.4060	177.1640	40	50	C_{30}-25-Norhopanes
19	482.4820	191.1790	40	50	C_{35} Triterpanes

All δ^{13}C values are reported in the standard "delta notation" relative to the Pee Dee Belemnite (PDB) where:

$$\delta^{13}C = \frac{\left(\dfrac{^{13}C}{^{12}C}\text{sample} - \dfrac{^{13}C}{^{12}C}\text{standard}\right)}{\dfrac{^{13}C}{^{12}C}\text{standard}} \times 1000$$

2.2.8 Compound specific isotope analysis (CSIA)

Compound specific isotope analysis (Hayes et al., 1990) of individual *n*-alkanes and resin-derived hydrocarbons was carried out on a Varian 3400 gas chromatograph (GC) connected to a Finnigan MAT 252 isotope-ratio mass spectrometer via a micro-volume combustion system. The GC was equipped with either a DB-1 or DB-5 fused silica column (25 m or 50 m x 0.25 mm ID; 0.2 μm film thickness) and the sample (in hexane) was injected into an SPI injector at 50 °C. During the initial GC oven hold time of 2 min. the injector was heated to 300 °C at 150 °C min^{-1} and then held at this temperature. The GC oven was programmed to 150 °C at 10 °C min^{-1}, then to 300 °C at 3 °C min^{-1}. Upon elution, the individual compounds were quantitatively converted to CO_2 and H_2O in the combustion reactor (CuO, 900 °C, 3 h) and after removal of water the isotopic composition of the CO_2 was measured. Perdeuterated C_{20} and C_{36} internal standards of known ^{13}C isotopic composition were used to check calibration. δ-values were determined using the manufacturer's software which corrected for background contributions, partial separation of isotopic species on the chromatographic column, and the contribution of [17]O.

2.2.9 Miscellaneous measurements

Measurements in respect of total sulphur, organic sulphur, vitrinite reflectance and palynological description for sediments were carried out by Coal Research Ltd., New Zealand and AMDEL Laboratories using accepted standard procedures. Palynological description of the Maniguin coal was provided by Dr. Clinton Foster (AGSO).

2.2.10 Calculation and data presentation procedures

Biomarker compounds were identified in GCMS chromatograms by comparison with published chromatograms (Peters and Moldowan, 1993 and references therein) and by observation of their response in the different channels. (e.g., oleananes respond in the m/z 412 → 191 chromatogram but not in the m/z 412 → 369 MRM-GCMS chromatogram whereas bicadinanes and hopanes respond in both). Moldowan et al. (1991) reported the presence of a triterpane with the same retention time as oleanane in oils of Prudhoe Bay, Alaska. Although the structure of this "impostor" compound was not then known, it could be distinguished from oleanane because it produced an M+ - 43 fragment (m/z 369) due to loss of an isopropyl group. This compound, which is probably lupane (Rullkotter et al., 1994), may have increased the apparent oleanane/hopane ratio for some of oils studied. The effect is not large for oils with abundant oleanane however, and no correction for it's presence was attempted. Where the oleanane content was low, the m/z 412→369 metastable transition was examined to ensure that oleanane isomers were primarily responsible for the peak observed.

Calculation of biomarker source and environment parameters generally follows the practice of Peters and Moldowan (1993). Peak area ratios are used in preference to absolute concentrations because they a) can be measured with greater precision b) can be placed in context with published

values and c) are equally useful in observing trends, which is the main purpose of this work. However, it is recognised that ratios such as oleanane/hopane can reflect changes in either the numerator or denominator, creating some ambiguity in the interpretation. Hence, wherever possible, and especially for the work described in chapter six, absolute biomarker concentrations were used to support and confirm interpretations based on peak area ratios. Different biomarker and isotope parameters are required for the work covered in each chapter and descriptions of their derivation are given therein.

The work described in chapter six required some estimate of the absolute concentrations of hopanoid and oleanoid biomarkers to be made. A full quantitative determination could not be carried out because pure standard compounds were not available. However, hopanoid and oleanoid concentrations could be estimated for the Buller coal extracts because the compounds were abundant enough in these samples to be observed in GC-FID gas chromatograms. The concentrations were determined by comparison of the GC peak areas to that of a trideuterated 3-methylcholestane external standard (Chiron, 10 µg added per 1 mg saturates) and used to calibrate the MRM-GCMS procedures (i.e., it was assumed that the GC-FID response factors were the same for the compounds in question and 3-methylcholestane). Because steranes were not visible in GC-FID chromatograms of the Buller Coals the GCMS analyses could not be calibrated for steranes in the same manner. Hence, the concentration of C_{27} sterane isomers in other samples was calculated by assuming an MRM-GCMS response (m/z 372→217) equivalent to the trideuterated 3-methylcholestane internal standard (m/z 389→234).

In the absence of suitable reference materials, aromatic oleanoids (chapter six) were identified by comparison of relative retention times and mass spectra to published data (Ellis et al., 1996; Chaffee and Fookes, 1988; Chaffee and Johns, 1983; Stout 1992 and references therein). The concentrations were estimated by comparing the peak area in the GCMS

total ion chromatogram to the total area, including the unresolved envelope between the TIC trace and the baseline. The total area was then equated to the mass of total aromatic hydrocarbons as determined gravimetrically and the mass of individual compounds calculated. All concentrations were normalised to the TOC content of the sample and are expressed as mg g^{-1} (ppm) TOC. Trimethylnaphthalene ratios are formed from peak areas rather than absolute amounts. However, the ratio of saturated to aromatic oleanoids calculated for the Buller coals is the concentration ratio of oleananes and oleanoid triterpanes to the sum of octahydro-, tetrahydro- and dimethylpicenes. The dibenzothiophene/phenanthrene ratio (chapter six) is the ratio of peak areas in m/z 184 and 178 chromatograms and is corrected for relative response as described in Hughes et al. (1995).

The overall precision for measurement of saturated biomarker ratios and absolute concentrations estimated from replicate analyses of a mixed oil standard (AGSOSTD oil, unpublished results) are ± 8% and ±12% respectively (RSD, n=6). The precision (RSD) for oleanane/hopane and oleanane (μg g^{-1} TOC) are ± 6% and ± 11% respectively based on replicate analyses of the Buller coals.

For the work described in chapter five, separate GCMS runs on dilute and more concentrated sample aliquots were used to measure bicadinane and sterane isomer distributions respectively. This avoided the problem encountered in preliminary work where the bicadinane isomer distribution was distorted by overloading, leading to erroneously low values for bicadinane maturity indicators.

CHAPTER 3: THE BIOMARKER AND CARBON ISOTOPE COMPOSITION OF SOME TERRIGENOUS OILS

3.1 Introduction

In this chapter, the biomarker and *n*-alkane isotope compositions of 32 crude oils from Southeast Asia, China, New Zealand, Australia and the USA are reported and discussed. The purpose is to provide internally consistent and high resolution biomarker/isotope data for a set of terrigenous oils from a variety of source rock depositional environments.

In order to elucidate the biomarker and isotope composition as completely as possible, the oils were analysed by high resolution GCMS and carbon isotope methods, viz., metastable reaction monitoring GCMS (MRM-GCMS) and gas chromatography-isotope ratio mass spectrometry (GC-IRMA). The results are interpreted in terms of the source-rock depositional environment for each oil, as judged from published geological and geochemical information. This *a-priori* assesment is necessary as a prelude to an assessment of the influence of depositional environment on the occurrence and abundance of land-plant biomarkers and the carbon isotope composition. The six environments in the classification scheme are: Fluvio-Deltaic (FD), freshwater transitional (TR), lacustrine (LAC), saline lacustrine (SAL), marine deltaic (MD) and marine carbonate (MC). This scheme is based on those of Robinson (1987) and Mello et al. (1988) with the addition of the TR designation to describe a freshwater marginal setting (e.g., shallow lacustrine). All but one of the above oils are derived from Tertiary-age source rocks containing angiosperm organic matter. However, three further FD oils from the Gippsland Basin were analysed for the carbon isotope composition of their *n*-alkanes. This was done in order to better elucidate the influence of conifer vs. angiosperm source type on the carbon isotope composition.

n-alkane isotope profiles were also measured for some deltaic sediments from the South Sumatra Basin (Indonesia) and coals from the Bulller Basin (New Zealand).

3.2   Samples

As discussed above, a classification of the source rock depositional environment for each oil was made on the basis of the published geological and geochemical information. This classification is shown in Table 3.1. Oils generated from Tertiary marine carbonates (MC) are not common in Southeast Asia and the only examples available for this study were from the North Palawan Basin. It should be noted that the source rocks for these oils have not been identified and that there are some unusual features of their molecular and isotopic composition with respect to other carbonate-derived oils (e.g., very heavy carbon isotope compositions: Palmer, 1984; Williams et al., 1992b). Most of the oils analysed originate from Southeast Asia, Southern China and New Zealand (Fig. 3.1) but two oils from saline lacustrine facies in the Uinta Basin (USA) were also included.

In order to emphasise source effects, highly biodegraded oils and those of unusually low or high maturity were not included in the sample set. However, the LAC 3 and FD 7 oils do show a partial depletion of the short chain n-alkanes, corresponding to light biodegradation, or level two on the scale of Peters and Moldowan (1993). Neither biomarker nor n-alkane isotope composition should be affected at this level (Palmer, 1984; Sofer, 1984).

n-alkane isotope profiles were also measured for four Ancient sediment samples from the Buller Basin (NZ) and six from the South Sumatra Basin (Indonesia).

Table 3.1   Classification of depositional setting, location and age of crude oils analysed for biomarkers and carbon isotopes.

Number/Label	Name	Basin	Probable Age of Source
Fluvio-Deltaic (FD)			
FD 1	Conf.	Tarakan	Miocene ?
FD 2	Conf.	Tarakan	Miocene ?
FD 3	Conf.	Ardjuna	Oligocene
FD 4	McKee	Taranaki	Eocene
FD 5	Maui-1	Taranaki	L. Cretaceous
FD 6	Conf.	Ardjuna	L. Oligocene
FD 7	Conf.	Ardjuna	L. Oligocene
FD 8	MST-11	Visayan	L.Cretaceous?
FD 9	Conf.	South Sumatra	Oligocene
FD 10	BS-OS-01	SE Luzon	Miocene ?
FD 11	Reina Regente	Visayan	L.Cretaceous?
FD 12	Conf.	South Sumatra	Oligocene
FD 13	Lufa Seep	Papuan	Tertiary
FD G*	Dolphin	Gippsland	L. Cretaceous
FD H*	Halibut	Gippsland	L. Cretaceous
FD C*	Basker	Gippsland	L. Cretaceous
Transitional (TR)			
TR 1	Leyte Seep	Visayan	Miocene
TR 2	Leyte Seep	Visayan	Miocene
TR 3	Conf.	Pearl River Mouth	Eocene
Lacustrine (LAC)			
LAC 1	Minas	Central Sumatra	Eocene-Oligocene
LAC 2	SE Balam	Central Sumatra	Eocene-Oligocene
LAC 3	Duri	Central Sumatra	Eocene-Oligocene
Saline Lacustrine (SAL)			
SAL 1	Bluebell	Uinta	Eocene
SAL 2	Redwash	Uinta	Eocene
SAL 3	Xiang-10	Dongting	E. Tertiary/L.Cretaceous ?
Marine Deltaic (MD)			
MD 1	Conf.	N.Palawan	E. Tertiary/L.Cretaceous ?
MD 2	Waitangi Seep	East Coast	Late Cretaceous?
MD 3	Kora	Taranaki	Paleocene
Marine Carbonate (MC)			
MC 1	Linapacan-1	N.Palawan	E. Tertiary/L.Cretaceous ?
MC 2	Nido-1	N.Palawan	E. Tertiary/L.Cretaceous ?
MC 3	Galoc-2	N.Palawan	E. Tertiary/L.Cretaceous ?
MC 4	Octon-1	N.Palawan	E. Tertiary/L.Cretaceous ?

* Gippsland Basin oils were analysed for *n*-alkane isotopes only.
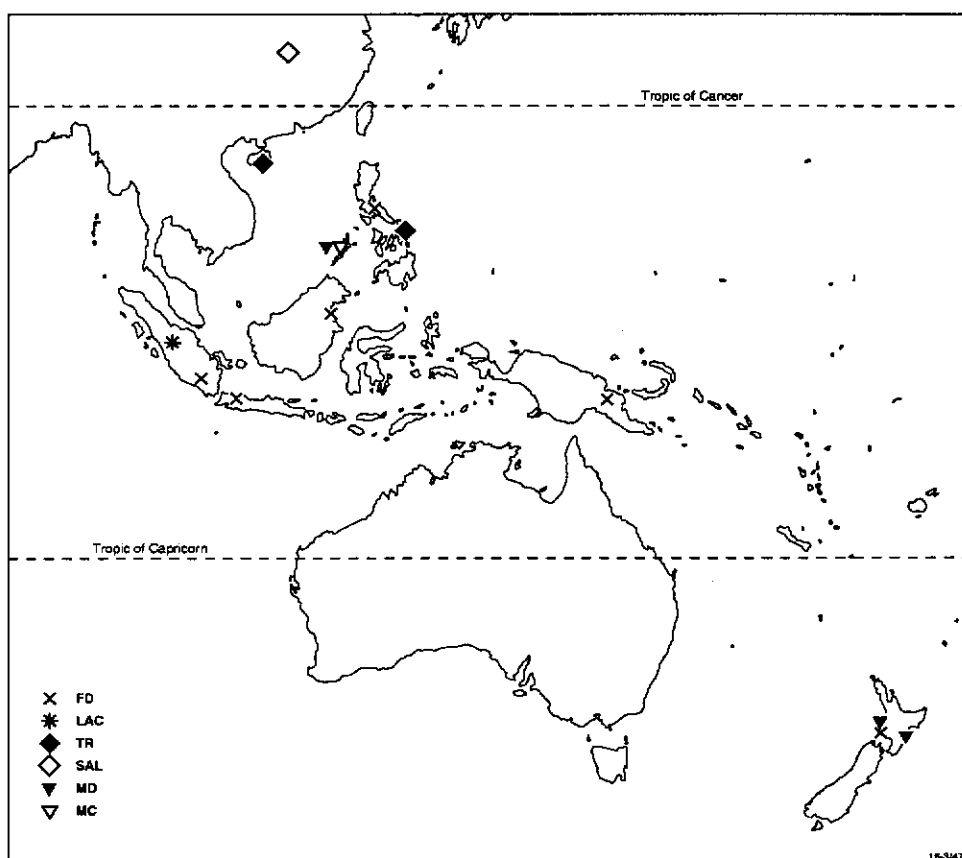
Figure 3.1   Geographic origin of oils used for the work described in this chapter (excluding the Gippsland Basin oils used for isotope work only and SAL oils from the Uinta Basin (USA)). Symbols correspond to more than one oil in most cases. See Table 2.1 for details.

Details of these samples are given in Table 2.2 and biomarker data are discussed in chapters five and six. Briefly, the Buller coals are stratigraphically equivalent to coals in the Taranaki Basin which are considered to be the source of the McKee oil (FD 4; Killops et al., 1994b). The samples are from a 10 metre thick section which experienced a seawater infusion during early diagenesis and the organic matter consists primarily of bacterially reworked angiosperm plant tissues. The maturity is equivalent to the onset of oil generation (vitrinite reflectance:R_0 0.6 - 0.7). The samples from the South Sumatra Basin are coals and shales deposited

during several million years development of a Tertiary deltaic sequence and in terms of thermal maturity they bracket the onset of oil generation (vitrinite relectance from 0.6 to 0.9 %). Once again, the organic matter type is dominantly bacterially reworked angiosperm remains, but the shales at 1802 m and 2069 m show a contribution from marine algal matter as well. In the case of the 1802 m sample the marine contribution is major while it is minor for the sample from 2069 m (see further details in chapter six).

n-alkane isotope profiles were also generated for three oils from the Gippsland Basin (FD G, Dolphin, FD H, Halibut, and FD C, Basker, Table 2.1). These oils differ from the oils in the main sample set in that they originate from a source rock of late Cretaceous age containing coniferous organic matter. They were not analysed for biomarkers as part of the present study but their biomarker composition is known from published and proprietary studies (AGSO/Geomark Research Ltd., "Oils of Oz" report, unpublished; Philp et al., 1981; Shanmugam, 1985)

3.3   Results

3.3.1   Biomarker composition

The distribution of n-alkanes, pristane and phytane in oils representative of each depositional setting is shown in Fig. 3.2. The shape of the n-alkane abundance profiles reflect both maturity and source effects (Peters and Moldowan, 1993), with waxy alkanes being dominant in both low maturity FD oils (e.g., FD 9) and moderate maturity lacustrine oils (LAC 1), whereas lighter n-alkanes are dominant in marine and high maturity deltaic oils. As expected, pristane/phytane is high for the FD oils, low for the MD and MC oils and intermediate for the TR oils. These data confirm that the sample set has the breadth of maturity and source type needed for a robust evaluation of the factors controlling land plant biomarker occurrence.
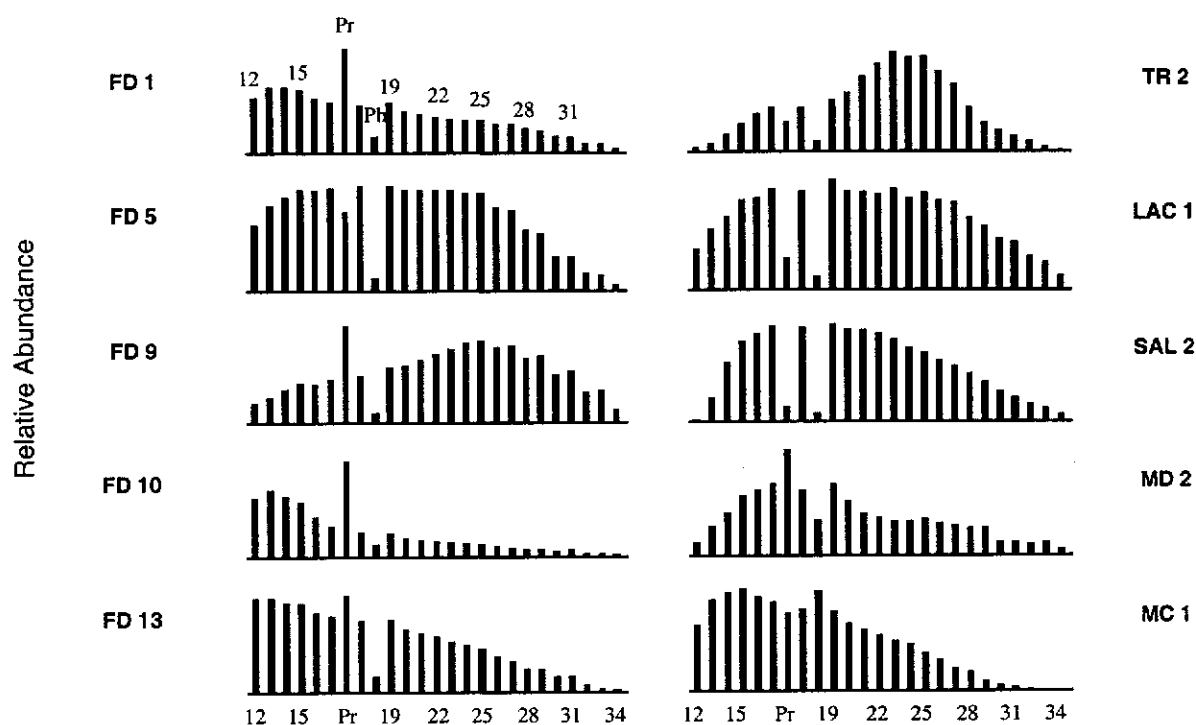
Figure 3.2   Distribution of C_{12}-C_{34} n-alkanes, pristane (Pr) and phytane (Ph) in selected crude oils (Table 3.1).

MRM-GCMS chromatograms for typical FD, TR, SAL and MC oils are shown in Fig. 3.3 and a peak annotation key is given in Table 3.2. The variation within and between classes of many of the commonly used biomarker parameters is shown in Fig. 3.4 (the parameters are defined in Table 3.4).

All of The FD oils contain numerous triterpanes of higher plant origin such as oleananes, C_{30} oleanoid triterpanes and bicadinane isomers (Figs. 3.3 and 3.4). The ratio of oleananes ($\alpha + \beta$) to 17α, 21β hopane has been called the "oleanane parameter" (Ekweozor and Telnaes, 1990) and "oleanane index" (Peters and Moldowan, 1993) and is presented for the oils in this study in Table 3.3 and Fig. 3.4. Some values of this index are slightly inflated by the presence of a co-eluting non-oleanoid triterpane marked as "?" in Fig. 3.5. This compound is probably lupane (Rullkotter et al., 1994).

Figure 3.3 (A-D)

Figure 3.3 (E-H)

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SAL 3
C_{30} 414 → 217 RI 2

C_{29} 400 → 217 20S $\alpha\alpha\alpha$ 20R + S $\alpha\beta\beta$ RI 100 $\beta\alpha\beta\alpha$ 20R $\alpha\alpha\alpha$

C_{28} 388 → 217 20S $\alpha\alpha\alpha$ 20R + S $\alpha\beta\beta$ RI 72 $\beta\alpha\beta\alpha$ 20R $\alpha\alpha\alpha$

C_{27} 372 → 217 20S $\alpha\alpha\alpha$ 20R + S $\alpha\beta\beta$ RI 62 $\beta\alpha\beta\alpha$ 20R $\alpha\alpha\alpha$

C_{30} 414 → 231 RI 36 20R 4α(Me) — 24 (Et) + Dino

49:50 54:10 58:30 1:02:50 1:07:10 1:11:30 1:15:58
Time (hour)

MC 1
C_{30} 414 → 217 RI 14 $\beta\alpha$ $\beta\alpha\alpha\alpha$ 20S 20R + S $\alpha\beta\beta$ 20R $\alpha\alpha\alpha$

C_{29} 400 → 217 20S $\alpha\alpha\alpha$ 20R + S $\alpha\beta\beta$ RI 100 $\beta\alpha$ $\beta\alpha$ 20R $\alpha\alpha\alpha$

C_{28} 388 → 217 20S $\alpha\alpha\alpha$ 20R + S $\alpha\beta\beta$ RI 81 $\beta\alpha$ $\beta\alpha$ 20R $\alpha\alpha\alpha$

20S $\alpha\alpha\alpha$ 20R + S $\alpha\beta\beta$ $\beta\alpha$ 20R $\alpha\alpha\alpha$ C_{27} 372 → 217 89 RI $\beta\alpha$

C_{30} 414 → 231 RI 21 20R 4α(Me) — 24 (Et) + Dino

49:50 54:10 58:30 1:02:50 1:07:10 1:11:30 1:15:50
Time (hour)

Figure 3.3 (I) and (J)

Figure 3.3	Mass chromatograms (MRM-GCMS) showing responses from triterpanes and steranes in representative oils: Traces A-E show triterpanes, F-J steranes for each oil. Refer to Table 3.2 for a key to peak annotation. Annotations show the carbon number, metastable transition monitored and the scale factor (larger number = greater relative peak height). RI = relative intensity.

Table 3.2   Peak annotation key for MRM-GCMS chromatograms.

Label	Definition
1,2,3,4,5,6,7	C_{30} Triterpanes of unknown structure - see text and Table 3.5
"$\alpha\alpha\alpha$" and "$\alpha\beta\beta$"	For regular steranes, configuration at the 5(H), 14(H) and 17(H) positions
"$\alpha\beta$" and "$\beta\alpha$"	Configuration of H for the regular hopanes at the 17 and 21 positions or ($\beta\alpha$) diasteranes
29,30 BNH	29,30-Bisnorhopane (dinorhopane)
Dino	Dinosterane isomer (4α,23,24 trimethyl cholestane)
γ	Gammacerane
4α(Me)-24-(Et)	4α-Methyl-24-ethyl cholestane
MeT, MeW, MeT1, MeR	Ring methylated analogs of the corresponding bicadinanes (see below)
neo	18α(H) 30-norhopane (C_{29}Ts)
30-nor	C_{30} Member of 30-norhopane series
20S and 20R	Sterane epimeric configuration at C_{20}
T, T1, R	C_{30} Bicadinanes of proven or inferred *trans-trans-trans* configuration
T_m	22,29,30-Trisnorhopane (17α(H))
Tri	Tricyclics (cheilanthanes)
T_s	22,29,30-Trisnorneohopane (18α(H))
V,W,W1,W2	C_{30} Bicadinanes of proven or inferred *cis-cis-trans* configuration

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Table 3.3   Key biomarker parameters and carbon isotope ratios for the oil set. The parameter definitions are given Table 3.4.

Fluvio-deltaic (FD) oils

Parameter	FD1	FD2	FD3	FD4	FD5	FD6	FD7	FD8	FD9	FD10	FD11	FD12	FD13
Pristane/phytane	6.3	6.7	8.0	7.5	6.1	6.8	5.8	6.6	8.0	7.0	8.0	2.1	5.9
Oleanane/C_{30} hopane	0.76	1.0	0.31	0.61	0.07	0.33	0.30	0.53	0.69	1.1	0.35	1.0	0.70
Oleanoid triterpanes/oleanane	2.4	2.4	2.9	1.2	2.6	4.2	3.4	1.5	2.9	0.79	3.5	2.4	1.9
Bicadinanes/C_{30} hopane	30	9.9	94	2.5	1.7	20	63	0.5	229	7.1	0.3	190	7.8
%C_{27} Steranes	5.6	8.3	9.1	9.3	9.9	10.6	16.7	18.1	18.9	19.0	19.6	22.2	23.6
C_{30} 4-MeSt(R)/C_{29} DesMeSt(R)	0.04	0.05	0.14	0.13	0.29	0.13	0.20	0.07	0.18	0.14	0.16	0.21	0.14
% C_{30} Desmethyl steranes (24-*n*-propyl), C_{30} Index	<1	<1	<1	<1	1.6	<1	<1	<1	<1	<1	<1	<1	<1
Gammacerane/C_{30} hopane	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
C_{29} 30-Norhopane/C_{30} hopane	0.65	0.43	0.44	0.67	1.02	0.41	0.74	0.51	0.36	0.57	0.44	0.34	0.36
Hopanes/steranes	0.69	0.72	3.6	3.3	0.72	2.2	1.7	1.0	5.7	0.68	0.56	1.0	0.34
% (C_{27}+C_{30}) Steranes	7.0	8.1	8.4	11.1	12.5	11.0	15.5	19.3	13.0	19.5	18.7	25.2	24.5
$\delta^{13}C_{males}$	-31.2	-28.9	-31.0	-29.4	-28.3	-27.6	-28.7	-30.1	-30.8	nm	-30.5	-27.3	-27.9
$\delta^{13}C_{sats}$	-30.1	-29.0	-29.0	-28.7	-27.5	-26.9	-27.6	-28.4	-29.1	nm	-29.8	-25.0	-26.1
C_{17} Isotope anomaly	0.08	-0.14	-0.1	0.2	0.1	0.0	1.7	1.8	1.4	-0.6	1.7	1.1	0.14

Table 3.3   (Cont.)

Transitional (TR), Lacustrine (LAC), Saline lacustrine (SAL), Marine Deltaic (MD) and Marine Carbonate (MC) oils

Parameter	TR1	TR2	TR3	LAC1	LAC2	LAC3	SAL1	SAL2	SAL3	MD1	MD2	MD3	MC1	MC2	MC3	MC4
Pristane/phytane	3.1	2.6	1.6	2.4	1.8	2.0	1.1	1.7	0.80	1.6	2.6	2.8	0.71	0.72	0.91	0.97
Oleanane/C_{30} hopane	0.28	0.17	0.14	0.08	0.03	0.02	0.12	<0.05	0.09	0.38	<0.05	0.14	0.24	0.43	0.29	0.30
Oleanoid triterpanes/oleanane	0.68	0.69	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.42	0.30	0.61	0.35
Bicadinanes/C_{30} hopane	2.3	1.7	0.8	1.2	<0.1	1.0	1.0	2.1	<0.1	1.3	<0.1	0.2	0.3	0.5	0.7	1.4
%C_{27} Steranes	16.7	21.6	33.4	30.4	41.5	48.2	24.7	25.2	27.1	34.5	37.5	42.2	31.4	32.9	35.2	39.3
C_{30} 4-MeSt(R)/C_{29}DesMeSt(R)	1.8	2.6	4.8	2.7	2.1	1.5	0.41	0.24	0.27	0.35	0.25	0.12	0.08	0.06	0.23	0.22
% C_{30} Desmethyl steranes (24-*n*-propyl), C_{30} Index	<1	<1	<1	<1	<1	<1	<1	<1	<1	2.9	3.7	28.4	1.1	4.4	1.3	1.5
Gammacerane/C_{30} hopane	0.05	0.02	<0.05	<0.05	<0.05	<0.05	0.54	<0.05	0.36	0.06	<0.05	<0.05	0.03	<0.05	0.05	<0.05
C_{29} 30-Norhopane/C_{30} hopane	1.07	1.01	0.50	0.45	0.86	0.70	0.48	0.71	0.64	0.70	0.60	0.67	1.97	2.16	2.08	1.60
Hopanes/steranes	6.9	7.4	1.8	3.4	5.3	4.2	1.4	0.48	0.13	0.40	0.48	0.16	0.60	0.57	0.39	0.52
% (C_{27}+C_{30}) Steranes	20.0	25.3	37.8	42.4	45.0	63.8	28.4	29.7	27.8	40.1	37.9	57.5	34.8	37.1	37.1	43.6
$\delta^{13}C_{rm\text{-}sks}$	nm	-31.9	-28.7	-28.3	-23.6	-25.6	-30.7	-32.1	-30.4	-22.4	-30.0	-25.2	-18.3	nm	-18.5	-22.7
$\delta^{13}C_{Sat}$	nm	-30.7	-28.3	-25.7	-22.6	-24.9	-31.2	-32.5	-28.5	-22.0	-29.1	-23.8	-17.9	nm	-18.7	-21.2
C_{17} Isotope anomaly	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm

nm: not measured
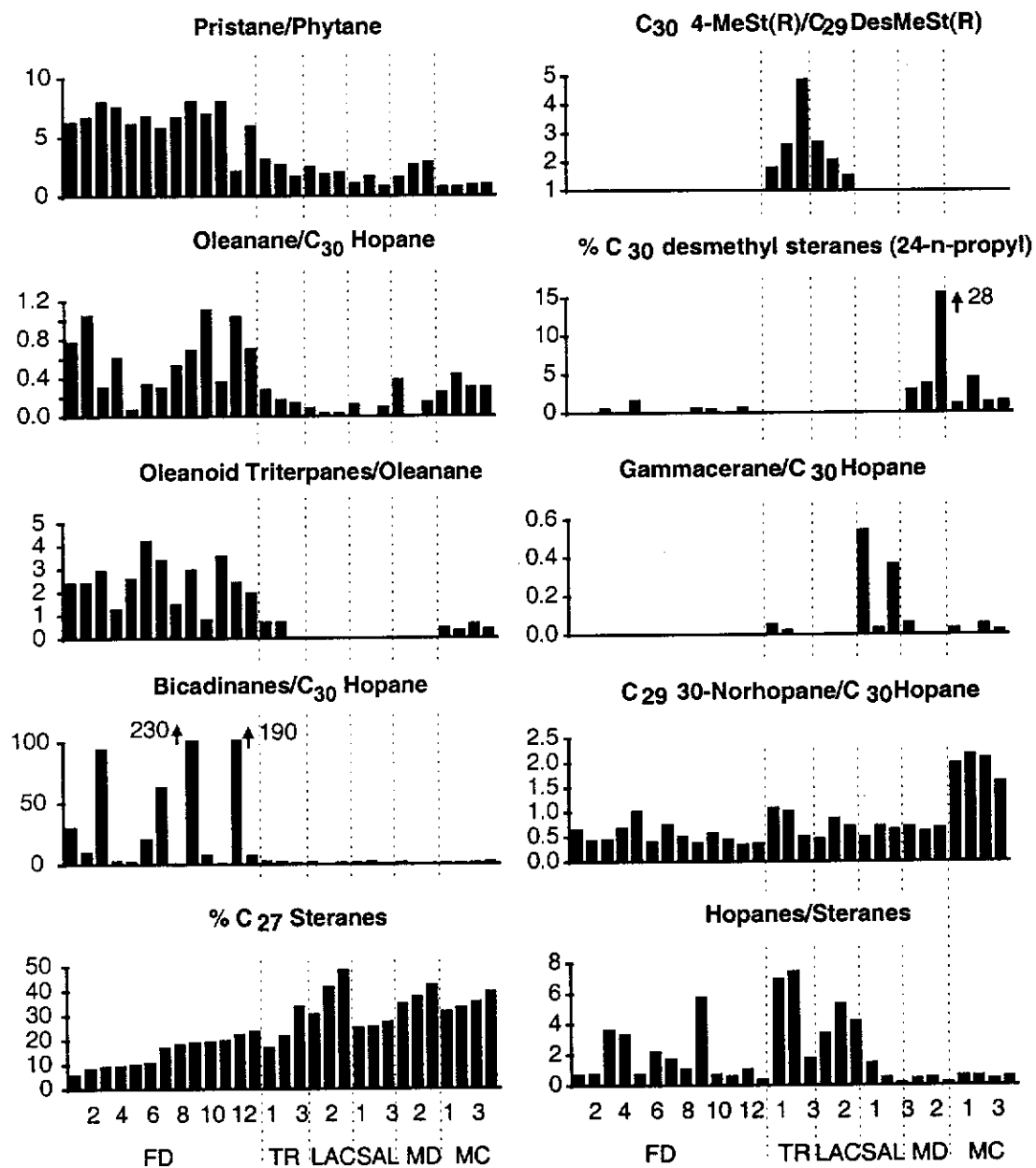
Figure 3.4 Variation in selected biomarker parameters as a function of depositional setting. Parameter definitions are given in Table 3.4.

Table 3.4   Definition and method of calculation of biomarker and isotope parameters. Peak areas from the appropriate MRM-GCMS chromatograms were used except where otherwise noted.

Parameter	Definition
Pristane/Phytane	Peak area ratio from gas chromatogram
Oleanane/C_{30} Hopane	18α+18β-Oleanane/17α,21β-hopane
Oleanoid Triterpanes/Oleanane	Sum of seven oleanoid triterpanes/18α+18βOleanane [Refer to Fig. 3.3A, compound 5 is below detection limit in this sample)
Bicadinanes/C_{30} Hopane	Total bicadinanes/17α,21β-hopane
% C_{27} Steranes	C_{27} $\alpha\alpha\alpha$, and $\alpha\beta\beta$ steranes as a % of equivalent isomers for C_{27}-C_{29} desmethyl steranes.
C_{30} 4-MeSt(R)/C_{29}DesMeSt(R)	4α-methyl-24-ethyl cholestane (R)/24-ethyl cholestane(R)
% C_{30} desmethyl steranes (24-n-propyl), also called "C_{30} Index"	C_{30} $\alpha\alpha\alpha$, $\alpha\beta\beta$ and $\beta\alpha$ (dia) steranes as a % of equivalent isomers for C_{27}-C_{30} desmethyl steranes.
Gammacerane/C_{30} Hopane	Gammacerane/17α,21β-hopane
C_{29} 30-norhopane/C_{30} Hopane	C_{29} 17α, 21β, 30-norhopane/17α,21β-hopane
Hopanes/Steranes	Sum of (C_{27}-C_{34} 17α,21β hopanes + T_s)/Sum of C_{27} - C_{30} desmethyl steranes ($\alpha\alpha\alpha$, $\alpha\beta\beta$ and $\beta\alpha$ (dia))
% (C_{27}+C_{30}) steranes	Sum of % C_{27} and % C_{30} steranes defined above except in this case % C_{27} steranes calculated as % of C_{27}-C_{30} steranes.
$\delta^{13}C$n-alks	$\delta^{13}C$ for the n-alkane fraction, calculated from the sum of concentration weighted δ values for individual C_{12}-C_{34} n-alkanes (excluding n-C_{28})
C_{17} isotope anomaly	Difference between $\delta^{13}C$ value for n-C_{17} and the average of δ values for n-C_{16} and n-C_{18}

Although Smith et al. (1995) have now identified compound "2" among the oleanoid triterpanes as 5(4→3)abeo-3α(H),5β,18α-oleanane, the structures of the other compounds remain unknown. In the absence of confirmed structures (and hence formal nomenclature) it is difficult to correlate the occurrence of the oleanoid triterpanes in different reports. To alleviate this problem, retention indices were calculated using the C_{27} and C_{30} regular

hopanes as references. Table 3.5 lists these retention indices, along with those of the main bicadinane and methyl bicadinane isomers, and correlates the trivial nomenclature used here with that of earlier workers. As summarised in the table, some of the unknown compounds give an m/z 369 ion in their mass spectra while others do not. This feature probably arises from the presence of a pendant isopropyl group and has been used, together with elution order, to infer hopane, spiroterpane and lupane structures (Woolhouse et al., 1992; Armanios et al., 1994). The absence of a peak in the m/z 369 chromatogram should not, however, be considered proof of the absence of an isopropyl group as, for some molecular configurations, the loss may not occur readily under standard GCMS conditions. The oils show considerable variation in the pattern of oleanoid triterpanes and the two most common patterns are those shown in Fig. 3.5. As can be seen, the oil from PNG contains more of compounds one and six and less of compounds two and three compared to the oil from New Zealand.

Oleanoid triterpanes accompany oleanane in all of the FD oils and also occur in trace quantities in the MC oils. Their abundance relative to oleanane is variable (Fig. 3.4) and they were not detected at all in the LAC or MD oils, even though some of these contain substantial amounts of oleanane (e.g., MD1).

In keeping with the precedent set by Grantham et al. (1983) and continued by others since (Alam and Pearson, 1990; Murray et al., 1993, 1994a), trivial names were assigned to the seven bicadinanes and three ring-methylated bicadinanes detected most frequently in the oils. This nomenclature is used in Figs. 3.3 and 3.5 and for simplicity the trivial names of compounds W, T and R are retained, even though compounds "W" and "T" are now known to be cis-cis-trans and trans-trans-trans bicadinane respectively (Cox et al., 1986; van Aarssen et al., 1990b).
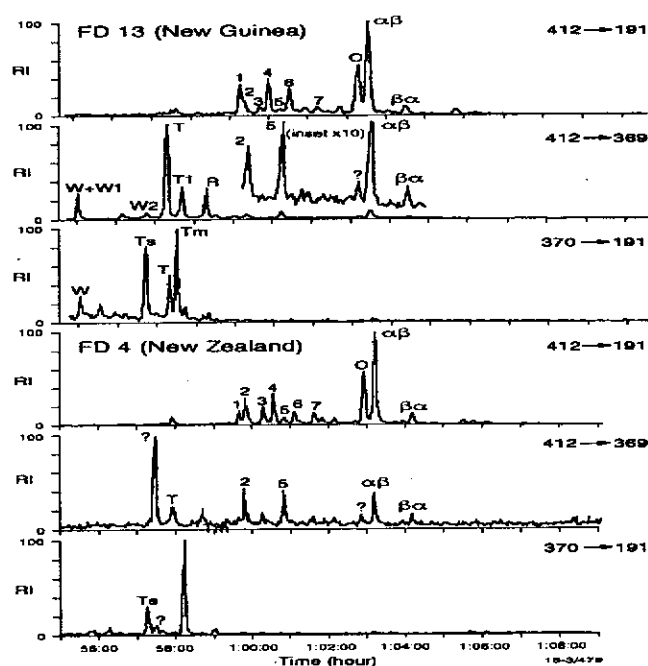
Figure 3.5   Partial MRM-GCMS chromatograms (expanded scale) showing oleanoid and other triterpanes in FD oils from Papua New Guinea (top) and New Zealand (bottom). The oleanoid triterpane region in the New Guinea oil has been expanded in the m/z 412→369 chromatogram to compensate for the dominance of this trace by bicadinanes. For the meaning of peak labels see Table 3.2. RI = Relative Intensity.

Table 3.5   Gas chromatographic retention indices (RI), based on the regular hopane series, and comparitive nomenclature for "oleanoid" and other triterpanes (HP Ultra 1, crosslinked methylsilicone column).

Peak	RI	Ref. 1	Ref. 2	Ref. 3	Ref. 4	412 → 369 ?[*]
C_{27} 18α(H)-Trisnorneohopane (T_s)	2636	A	6	18α(H)		No
C_{30} Bicadinane "T"	2686				29	Yes
C_{27} 17α(H)-Trisnorhopane (T_m)	2700	B	8	27		No
C_{31} Bicadinane "MeT"	2759				32	Yes
C_{30} Unknown 1	2830		9	F		No
C_{30} Unknown 2	2836	C	10	G	36	Yes
C_{30} Unknown 3	2862	D	11		39	Yes
C_{30} Unknown 4	2873	E	12	H	40	No
C_{30} Unknown 5	2894					Yes
C_{29} 17α(H),21β(H)-30-Norhopane	2900	F	13	29	41	No
C_{30} Unknown 6	2904	G ?	13	I ?		No
C_{30} Unknown 7	2924		15			Yes
18α(H)-Oleanane ("O")	2988	I	16	Olean	47	No
C_{30} 17α(H),21β(H)-Hopane	3000	K	17	30	49	Yes

1. Ekweozor and Udo, 1988; 2. Woolhouse et al., 1992; 3. Curiale and Lin, 1991; 4. Armanios et al., 1994. [*] Shows a peak in this mass chromatogram, yes or no.

Alam and Pearson (1990) used the label R' for a peak arising from co-elution of a bicadinane and a methyl bicadinane but MRM-GCMS analysis (as used here) allows deconvolution of the two peaks in the m/z 412→369 and 426→383 mass chromatograms (Fig. 3.3). Thus, the term R is used here to refer to the last eluting bicadinane and MeT to denote the coeluting methyl bicadinane. The names given to this compound and to "MeW" reflect an assumption that these compounds are ring methylated analogs of the *trans-trans-trans* and *cis-cis-trans* bicadinanes respectively. This is argued on the basis of their mass spectra, relative retention times and the covariance of the W/T and MeW/MeT ratios (van Aarssen et al., 1992a). Mass spectra for all of the compounds assigned trivial names were obtained during resin pyrolysis studies (Murray et al., 1994a) and again, by analogy with the spectra of "W" and "T", compounds V, W1, W2 and MeW are presumed to have the *cis-cis-trans* configuration and the remainder (T, T1, R, MeT, MeT1, MeR) the *trans-trans-trans* configuration. The term "total bicadinanes" used hereafter refers to the sum of the ten named compounds. The variation in total bicadinanes/C_{30} hopane ratio for the different classes of crude oil is shown in Fig. 3.4. This ratio varies over three orders of magnitude, even within the fluvio-deltaic group, and is much more variable than the oleanane/hopane ratio. In all cases the most abundant bicadinane isomer was compound "T" , i.e., the *trans-trans-trans* isomer, and ring methyl bicadinanes were also present. Only traces of bicadinanes were detected in the marine and lacustrine oils.

The chromatograms in Fig. 3F-J demonstrates the resolution of sterane homologs attained and Table 3.3 gives the resulting percentages of C_{27} and C_{30} desmethylsteranes. These data, although not directly related to the abundance of land plant markers, are essential in defining the depositional environment of the source rock (see discussion). MRM-GCMS is capable of detecting the small but significant amounts of the C_{30} homologs (24-*n*-propylcholestanes) which are diagnostic of a marine algal contribution to the source. This is shown in Fig. 3.6 which shows 24-n-propylcholestanes in three oils, all from the Taranaki Basin, New Zealand. Values of the C_{30}

sterane index (or %C_{30} steranes of the total C_{27}-C_{30} steranes) for all the oils analysed are given in Table 3.3.
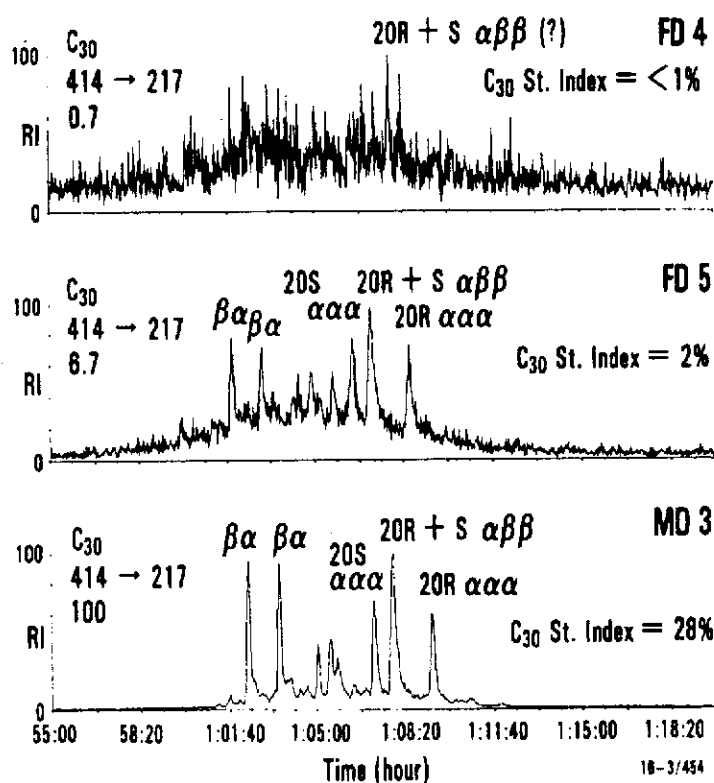
Figure 3.6   MRM-GCMS chromatograms showing 24-n-propyl cholestanes in three deltaic oils (two FD, one MD) from the Taranaki Basin, New Zealand. The minor offset between equivalent peaks in FD 5 and MD 3 is due to a slight change in chromatographic conditions. The C_{30} index is calculated as described in Table 3.4.

The TR and LAC oils all contain abundant 4α-methyl-24-ethyl cholestanes (Figs. 3.3H and 3.4) which are derived from sterols present in dinoflagellates, prymnesiophytes and/or freshwater macrophytes (Wolff et al. 1986; Volkman et al. 1990; Klink et al. 1992). The MAR and SAL oils also contain these compounds, but in smaller relative amounts, and they are accompanied here by 4α,23,24-trimethyl cholestanes (dinosteranes). It is difficult to reliably quantify 4-methyl steranes (including dinosteranes) in the FD oils due to

interference from 2- and 3-methyl isomers and higher plant triterpanes. However, none contain large amounts of these compounds.

3.3.2 Carbon isotopes

Although the main focus of this study was the carbon isotope composition of individual n-alkanes, $\delta^{13}C$ values were also measured on the saturate hydrocarbon fraction for some samples. A comparison of the concentration weighted average for the n-alkanes with the value for the whole saturate fraction then gives an indication of the carbon isotope ratio of the branched/cyclic fraction. This can be difficult to measure directly because of the practical difficulty in completely removing the n-alkanes from the saturate fraction. The results are depicted in Fig. 3.7 where it is seen that the saturate hydrocarbon fractions - and by implication the branched/cyclics - are typically enriched in the ^{13}C isotope relative to the n-alkanes. The exceptions are one FD, one MC and two SAL oils. One oil (LAC 1) has n-alkanes which are on average 2.5‰ lighter than the total saturates. The carbon isotope data obtained for LAC 1 and another lacustrine oil from the same basin are depicted in Fig. 3.8 where n-alkane isotope data are superimposed on the gas chromatograms of the saturate hydrocarbon fractions. This demonstrates the concept of the "n-alkane *isotope* profile" which can be used as a characteristic and complementary feature to the n-alkane *abundance* profile depicted in a gas chromatogram. Both the shape of the isotope profile and and it's absolute position on the $\delta^{13}C$ axis are important correlation features.

n-alkane isotope profiles for the oils in each class are shown in Fig. 3.9. All of the FD and TR oils and one of the LAC oils show a trend toward isotopically lighter values with increasing chain length. That is, the plots slope down from left to right (negative slope), the range from the shortest to longest chain alkanes being typically 2-4 ‰.
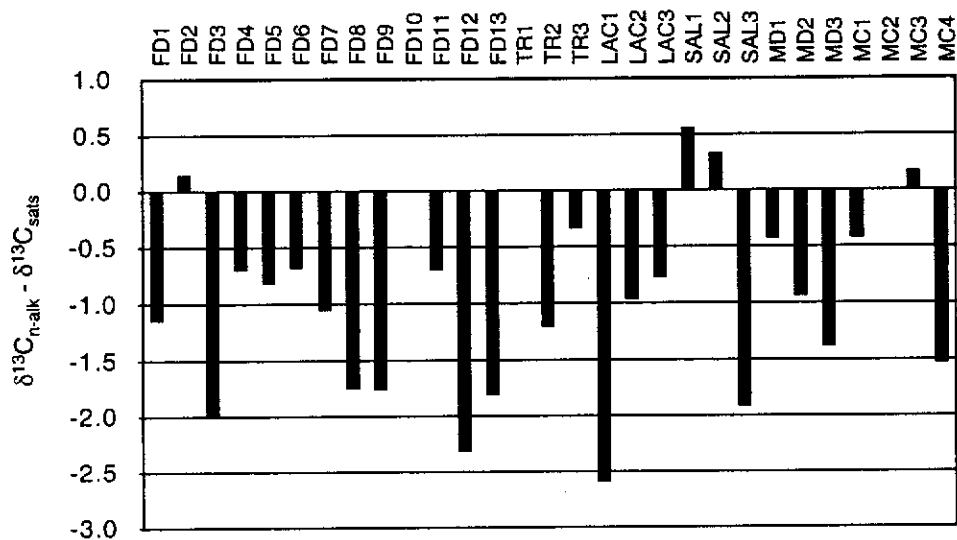
Figure 3.7   Comparison between bulk saturate and *n*-alkane fraction carbon isotope ratios for selected oils. $\delta^{13}C_{n\text{-alks}}$ is calculated as described in Table 3.4 and in the text.
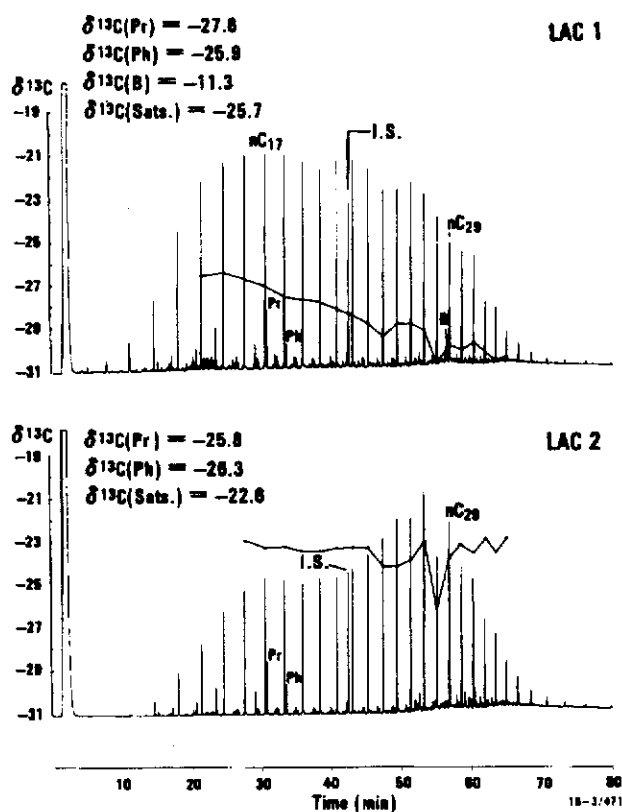
Figure 3.8   Gas chromatograms and isotope ratios for bulk fractions, isoprenoids and *n*-alkanes in two LAC oils from Central Sumatra. I.S. = internal standard, Pr = pristane, Ph = phytane, B = botryococcane. The $\delta^{13}C$ value for *n*-C_{28} is in error, probably due to a coeluting compound.
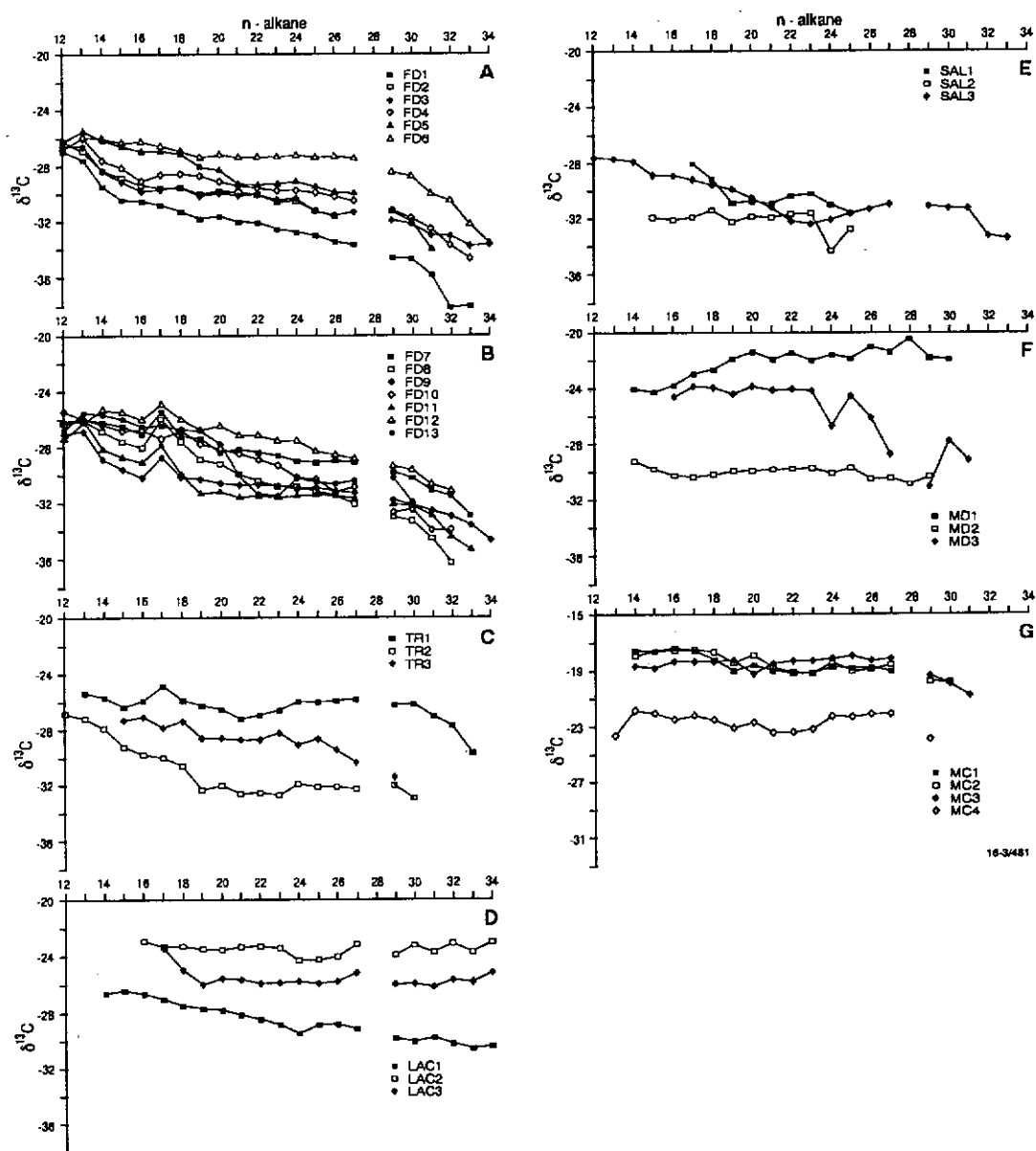
Figure 3.9   n-Alkane isotope profiles for oils of each class. The value for C_{28} has been deleted for most samples due to a systematic error encountered with this compound (e.g., see Fig. 3.8). This error did not occur with a later set of analyses, allowing C_{28} data to be obtained for samples such as MD 2. The FD class is split into two groups on the basis of the C_{27} sterane content (A) < 10 % and (B) > 10 % (see the text and Fig. 3.4). $\delta^{13}C$ values in ‰ vs. PDB.

The remaining MD, MC, LAC and SAL oils give profiles which are either flat or slope in the opposite direction. The data for the FD oils has been split into two groups to assist evaluation of the effect of source matter

type/depositional environment on the n-alkane isotope profile. The profiles for oils containing less than 10% C_{27} steranes and therefore exhibiting minimal marine influence appear in Fig. 3.9A, those for oils with more than 10% C_{27} steranes in Fig. 3.9B. A systematic error (subsequently found to be due to a co-eluting compound, see Dowling et al., 1995) prevented determination of the isotope value for nC_{28} in all but a few cases.

Three further oils from the Gippsland Basin (not part of the main study) were analysed for n-alkane isotopes to facilitate comparison between angiosperm and conifer derived oils. The results are shown in Fig. 3.10 and compared there with the data for one angiosperm and one mixed angiosperm/conifer derived oil from New Zealand. An n-alkane isotope profile generated from the average of individual compound responses for all angiosperm derived oils is also shown. n-alkanes in the conifer-derived Gippsland oils were found to be consistently and significantly enriched in ^{13}C (by up to 2 ‰) with respect to those in the angiosperm derived oils. Intermediate values were found for the Maui oil of mixed conifer and angiosperm origin.
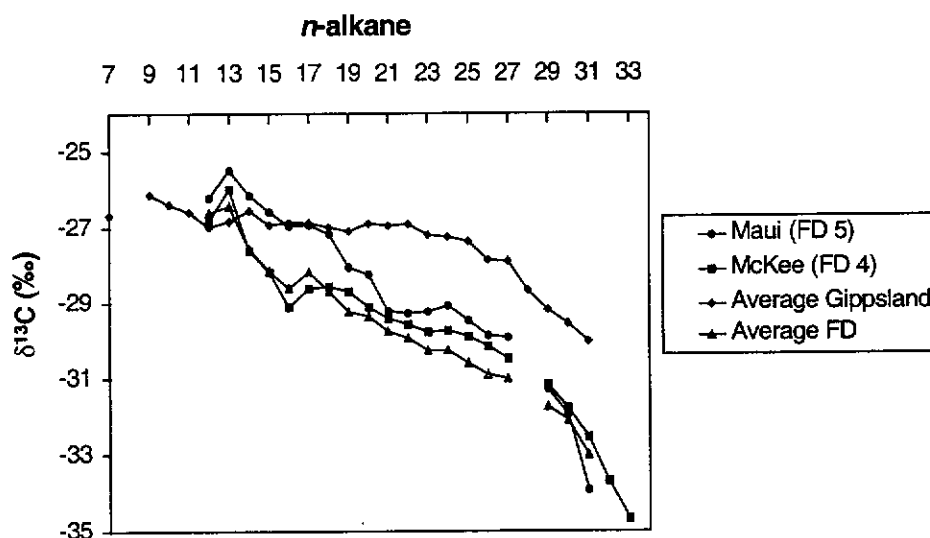
Figure 3.10 n-alkane isotope profiles for fluvio-deltaic oils of conifer (Gippsland), mixed conifer-angiosperm (Maui) and angiosperm (McKee, average FD) provenance. The Gippsland Basin oils are FD G, FD H and FD C while the the "average FD" set refers to all of the FD oils (Table 2.1) except the Gippsland, Maui, Perth Basin (FD P) and Brunei (FD B) oils.

Negatively sloping n-alkane isotope profiles were also obtained for extracts
of Ancient sediments from the Buller and South Sumatra Basins. Profiles for
the four Eocene coal samples from the Buller field are shown in Fig. 3.11
and those for the six South Sumatra Basin sediments in Fig. 3.12. All 10
samples yield negatively sloping n-alkane isotope profiles akin to those
obtained for the FD oils. The profiles for the Buller coals all fall within a
narrow window ca. 1 ‰ wide (note that the $\delta^{13}C$ scale is expanded relative to
the plots in Fig. 3.9).

The profiles for the South Sumatra Basin are also very similar to each other,
despite the long period of deposition and range of depths/thermal maturities
encompassed. The only divergent values were obtained for the shale from
1802 m. The biomarker data for this sample (see chapters five and six: gas
chromatograms showing the distribution of n-alkanes are also presented
there) shows a significant contribution from marine organic matter and, as
can be seen from Fig. 3.12, this sample also has slightly heavier $\delta^{13}C$ values
for the C_{18} - C_{24} n-alkanes. Isotope values for compounds below C_{18} were
difficult to obtain for some of the sediment samples, due to their low relative
abundance, and unfortunately this included the key value for nC_{17} in the most
marine influenced sample.
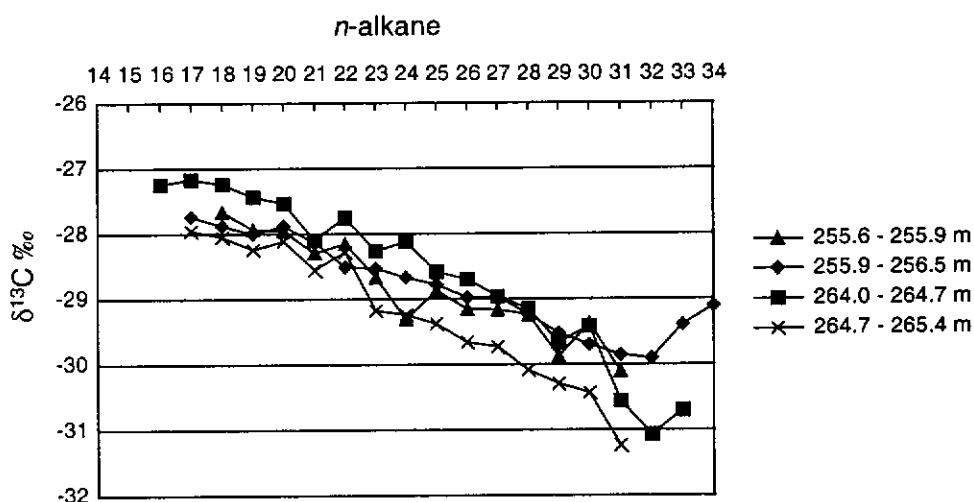
n-alkane

Figure 3.11   n-alkane isotope profiles for four samples through a 10 m section of the
Buller coals (see Table 2.2).

n-alkane

14 16 18 20 22 24 26 28 30 32 34

—×— 1742 m Coal
—♦— 1802 m Shale
—■— 1862 m Coal
—▲— 2026 m Coal
—*— 2069 m C. Shale
—●— 2309 m Coal
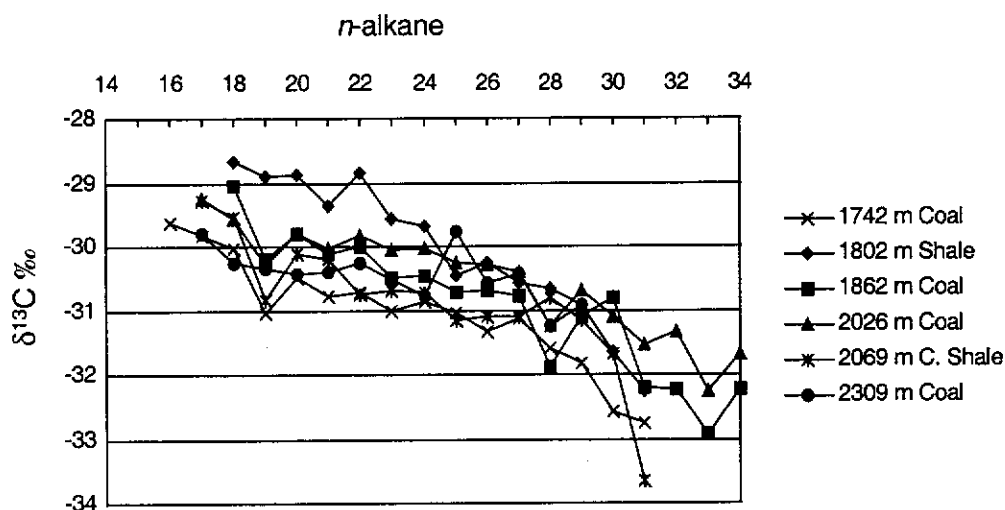
Figure 3.12   n-alkane isotope profiles for six sediment samples covering the range of 1742 - 2309 m depth in the GK well, South Sumatra Basin (see Table 2.2 for further sample details).

3.4   Discussion

3.4.1   Biomarker indicators of depositional environment

Before considering the influence of depositional environment and other factors on the distribution of land-plant markers in the oils, it is necessary to confirm that the other biomarker information is consistent with the *a priori* assignment of the oils to the FD, LAC etc. classes. The primary indicator of source matter type (and therefore indirectly of depositional environment) is the sterane distribution. High concentrations of C_{27} steranes are considered indicative of algal, especially marine, organic matter while a dominance of C_{29} steranes is often associated with land-plant pre-eminence among the source organics (Peters and Moldowan, 1993).

In general, the sterane distributions for the oils analysed here (Fig. 3.4) are consistent with their assigned depositional environments, with the highest C_{27} steranes concentrations in the marine and lacustrine oils. However, the occurrence in some of the FD oils of a reasonably high proportion of C_{27}

steranes raises the question as to whether there is a subsidiary algal influence on their source. This issue has significance from an exploration point of view because it has been argued by some that the best source facies in FD systems are the paralic or delta plain coals (Bal, 1994; Noble et al., 1991) and also that proximal marine deltaic shales can contribute significantly to oil generation (Katz, 1994; Noble et al., 1991). Despite this interest, the literature reveals no general agreement among petroleum geochemists as to the level of C_{27} steranes diagnostic of an algal contribution. The data presented by Huang and Meinschein (1979) and Moldowan et al. (1985) do however set an empirical limit of about 20 % C_{27} steranes in fully terrigenous oils, with values above this implicitly indicative of some algal contribution to the source rock. Among the present samples, only two FD oils contain more than 20 % C_{27} steranes, although a natural break appears between 10 and 17 % (Fig. 3.4). Other biomarker indicators of algal input, such as the C_{30} desmethyl steranes (marine algae) and ring A 4-methyl steranes (lacustrine algae) are no more abundant in oils above this break than in those below it. Hence, the C_{27} - C_{29} sterane distributions, are fully consistent with the general classification of the oils as FD, MD etc. They cannot be used, however to reliably infer a subsidiary marine influence on the source of a fluvio-deltaic oil.

In addition to ring methylated C_{30} steranes, the MD and MC and some FD oils contain C_{30} desmethyl steranes (24-n-propyl cholestanes) which Moldowan et al. (1990) have suggested are specific markers for marine chrysophyte algae. Oil MD 3 (Kora) has the highest C_{30} sterane index reported for any oil studied to date, and on this basis (as well as on it's heavy isotope signature) has been tied to a Paleocene marine deltaic shale (Killops et al., 1994b; Murray et al., 1994b). C_{30} desmethyl steranes were not detected in the LAC, TR or SAL oils. The traces present in several of the FD oils could arise from periodic marine incursion into a peat swamp source environment or by co-generation from interbedded marine shales. Alternatively, the presence of 24-n-propylcholestanes may be less specific for marine organic matter than is currently believed. Interestingly, the FD oils containing trace C_{30} desmethyl

steranes are not the ones with the highest proportion of C_{27} steranes. The FD oil with the highest proportion of C_{30} desmethyl steranes is the Maui-1 oil of the Taranaki Basin (FD 5). Others have suggested a marine influence on the source of this oil on the basis of it's high abundance of tricyclic terpanes (cheilanthanes) and C_{27} diasteranes (Cook, 1988; Killops et al., 1994b). However, in contrast to the results of Killops et al. (1994b), the C_{27}/C_{29} sterane ratio for this oil (Fig. 3.4) is no higher than for the other FD oils in which C_{30} steranes were not detected (e.g., FD 4 from the same basin). Killops et al. (1994b) used a "marine/terrestrial" index based on the relative abundance of C_{27}/C_{29} diasteranes measured in SIM-GCMS m/z 217 traces. This is less reliable than MRM-GCMS analysis of regular C_{27}/C_{29} steranes because of the high degree of peak overlap in the m/z 217 trace and the possibility of C_{29} and C_{27} dia- /regular sterane ratios not being equivalent.

What is the minimum extent of marine contribution to an FD oils which would be detectable via the C_{30} desmethylsteranes ? In their survey of 28 "open" marine oils, Moldowan et al. (1985) found an average C_{30} sterane index of 5% and a maximum of 11%. The quantitative detection limit for MRM-GCMS analysis of C_{30} steranes corresponds to a C_{30} sterane index of about 1% (the exact value depending on the overall concentration of steranes and the level of interferences). Hence, assuming that the marine component of a paralic source has the same content of C_{30} steranes as its open water equivalent, less than about 20:80 marine/terrestrial contribution to an FD source would not result in detectable C_{30} steranes. Nevertheless, much remains to be learnt about the relationship between marine biomass contribution and its expression in terms of the C_{30} desmethyl sterane content of source rocks and oils. For the present, the occurrence of these compounds in an FD oil can be considered reliable evidence of *some* marine contribution to the source, but not of it's magnitude. Furthermore, a failure to detect C_{30} desmethylsteranes in a deltaic oil does not prove the absence of a marine component.

Other biomarker features of the oils (Fig. 3.4) confirm the *a-priori* classifications. For example, gammacerane, considered a marker for

elevated salinity in the depositional environment (Peters and Moldowan, 1993), is abundant in two of the three SAL oils and was also detected in several of the marine oils, albeit in much lower concentration. A high ratio of the 30-norhopane to hopane is a feature commonly associated with oils derived from anoxic, marine carbonate source rocks and this feature is seen for the Palawan oils classified as "Marine Carbonate (MC)".

Total hopane/sterane ratio has proved to be one of the better discriminators between marine and non-marine oils in several studies (Mello et al., 1988; Moldowan et al., 1985; Zumberge, 1987). In the present survey, low hopane/sterane ratios were obtained for the marine (MD and MC) and two of the saline lacustrine (SAL) oils but low values were also obtained for some of the FD oils. This ratio is probably highly sensitive to variation in maturity (Peters and Moldowan, 1993 and references therein).

In summary, the biomarker data obtained by MRM-GCMS confirms the *a-priori* description of depositional environment assigned to each oil. While, there is some evidence of a subsidiary marine algal contribution to certain of the FD oils, the lack of such evidence does not preclude a marine influence during early diagenesis.

3.4.2 The distribution and abundance of land-plant biomarkers in relation to source-rock depositional environment

A key feature of the biomarker data for the oils is the almost universal presence of oleananes. The oleanane/hopane ratio has been used as an indicator of the scale of land-plant contribution to the source (Ekweozor and Telnaes, 1990) and it is not surprising that high values are obtained for some FD oils (Fig. 3.4). However, strictly speaking, the oleanane/hopane ratio is related not to the absolute content of land-plant biomass in the source but rather to the relative contributions from land plants and prokaryotes. Thus, assuming that heterotrophic bacterial activity responds to the availability of primary carbon, one might expect oleanane and hopane concentrations to be

linked. In fact, other workers have found a covariance of oleanane and hopane concentrations in Southeast Asian oils and sediments (van Aarssen et al. 1992a; Alam and Pearson, 1990). Furthermore, published and unpublished databases (Geomark Res. Ltd., C. Schiefelbein, personal communication) contain very few instances of the oleanane abundance in an oil exceeding twice that of hopane (except in the case of some severely biodegraded oils). This is so regardless of the inferred extent of land-plant contribution to the source. Finally, several of the marine and lacustrine oils in the present study have oleanane/hopane ratios higher than those of some FD oils (Fig. 3.4), despite a presumably lower higher plant contribution to the source. All of these observations suggest that factors other than the scale of the land-plant input affect the oleanane/hopane ratio of an oil. One of these factors may be the relative preservation of oleanoid vs. hopanoid skeletons during early diagenesis and this issue is revisited in chapter six.

Of course, a primary determinant of the oleanane content of a terrigenous oil is the relative abundance of angiosperms in the palaeoflora which in turn depends on the age of the source. Moldowan et al. (1994) reported on the relationship between source rock age, abundance of angiosperm fossils and the oleanane/hopane ratio (see Fig. 1.7). Their conclusions were that oils containing measurable oleanane (i.e., oleanane/hopane ratio > 0.03) were probably derived from Cretaceous or younger rocks while those with oleanane/hopane above 0.25 were very likely derived from Tertiary sediments. These conclusions are consistent with the results for the oils (Table 3.3) when considered in relation to the inferred ages of their source rocks. However, climate is also a factor in plant succession and must be considered when interpreting the oleanane/hopane ratio for any given oil. Since the angiosperm dominance began and remains greatest in the tropics (Crane and Lidgard, 1989; Lidgard and Crane, 1988), virtually all Tertiary, terrigenous oils of the tropics contain oleanane, whereas those of cooler regions often contain instead gymnosperm related diterpanes such as phyllocladane and isopimarane. Two of the FD oils in the set (FD 4 and 5) come from New Zealand, which experienced a cool-temperate to sub-tropical

climate during the Late Cretaceous/Early Tertiary (Mildenhall, 1980; Walley, 1992). FD 5 (Maui), considered to originate from Late Cretaceous coals/carbonaceous shales, contains abundant diterpanes (Killops et al., 1994b; Weston et al., 1989) and has the lowest oleanane/hopane ratio of the set. By contrast, FD 4 (McKee) from the same basin is derived from Eocene coals/shales containing mainly angiosperm debris, contains only traces of diterpanes, and has a much higher oleanane/hopane ratio (Czochanska et al.,1988; Killops et al., 1994b). Other NZ coals of Eocene age have no detectable oleanane and, along with their associated oils, show only the gymnosperm molecular signature (Czochanska et al., 1987). Thus, the oleanane content of an oil depends not only the extent of the land plant contribution to the source but also on a) source rock age b) paleoclimate during source rock deposition and c) conditions existing during early diagenesis as they mediate conversion of precursors to the saturated hydrocarbons.

Oleanoid triterpanes accompany oleanane in most, but not all of the oils analysed. Marine oils in particular show low ratios of oleanoid triterpanes to oleanane (Fig. 3.4). There are also several reports in the literature of marine deltaic oils or marine carbonate oils containing abundant oleanane but little or no oleanoid triterpanes (Ekweozor and Udo, 1988; Mello et al., 1988; Williams et al., 1992b). This suggests either that the two groups of compounds a) arise from different precursor compounds and perhaps from different plants, or b) arise from the same precursor compounds and plants but are affected differently by early diagenetic or transport processes (e.g. floating leaves vs. woody tissues deposited closer to the site of senescence). This is investigated further in chapter six.

Woolhouse et al. (1992) described the C_{30} triterpane distributions (oleananes, oleanoid triterpanes, bicadinanes) of oils from the Niger Delta, Beaufort-McKenzie Delta, Taiwan, Indonesia (Mahakam Delta) and New Zealand as "remarkably uniform". Nevertheless, the m/z 191 chromatogram presented for their Indonesian oil shows a different triterpane distribution to those from

Taiwan, New Zealand and Nigeria and this difference goes beyond that due to abundant bicadinanes (the main effect of which is to produce a peak eluting between T_s and T_m in the m/z 191 chromatogram). Much of the variation in these published chromatograms appears to be in the proportions of the different oleanoid triterpane isomers. Variation of this kind is also seen the chromatograms produced here (e.g. Fig. 3.5). The pattern observed for the oil from PNG, in which compounds lacking the pendant isopropyl group (or at least failing to show the m/z 412 → 369 transition in MRM-GCMS) are most prominent, is also evident in a chromatogram presented by Curiale and Lin (1991) for a lower delta plain shale from the Far East.

Several reports deal with the occurrence of isomeric bicadinanes in Asian oils and their origin from the "dammar" resins exuded by tropical angiosperms (van Aarssen et al., 1990a, 1992a; Alam and Pearson, 1990; Pearson and Alam, 1993). Although they are ubiquitous in oils of this region, their abundance relative to other biomarker compounds is highly variable (Fig. 3.4). There are several possible reasons for this variation, which is in stark contrast to the narrow range of concentrations seen for the oleananes:

Firstly the floristic source of the bicadinanes is more specific than that of the oleananes, which are considered to be general markers for the angiosperms. The high concentrations of bicadinanes in Southeast Asian oils undoubtedly results from the dominance of the resinous family Dipterocarpaceae in the Tertiary flora of the region (van Aarssen et al., 1992a; Ashton, 1982). However, van Aarssen et al. (1994) recently demonstrated that other, non-tropical, angiosperm families also produce the polycadinene resins which yield bicadinanes on maturation and predicted that bicadinanes would be found in oils from other parts of the world. This prediction is supported by a report of bicadinane occurrence in a hydrothermal petroleum from the USA (Clifton et al., 1990), by their detection here in an oil from New Zealand (Fig. 3.5) and by their presence in an oil of probable Jurassic age from the Perth Basin, Australia (Summons et al., 1995). Furthermore, Armanios et al. (1996) identified trace quantities of bicadinanes in a Jurassic sediment of the

Cooper Basin (Australia). Since the fossil record shows no evidence for the presence of dipterocarps in either Australia or New Zealand, and the paleoclimates would not have been conducive to them (Mildenhall, 1980), another tree family is implicated as the source of the bicadinanes in these samples.

A second possible reason for the variation in bicadinane/hopane ratios is dependence on source rock age. The consensus among paleobotanists is that the main source organisms, the dipterocarps, originated in western Malaysia during Late Cretaceous or Early Tertiary time but did not become widespread in the Southeast Asian region before the Miocene (Ashton, 1982; Lakhanpal, 1974). The pollen from *Dipterocarpus sp.* is one age control in a palynological zonation scheme used for non-marine stratigraphy in Thailand, the first occurrence there being in the earliest Miocene (Watanasak, 1989). The earliest known dipterocarp fossils (pollen) occur in the Oligocene of Borneo (Ashton, 1982 and references therein; P.S. Ashton, pers. comm.). Curiale and co-workers (1994) have recently reported the presence of bicadinane-generating resins in the Eocene of Myanmar (Burma), but it is not clear whether they arose from dipterocarps or from some other family of resinous angiosperms. Further work on the relationship between source rock age and bicadinane abundance is needed but, for the present, a high concentration (probably indicating a dipterocarp contribution to the source) is defined as total bicadinane/C_{30} hopane > 10. This is also the approximate relative concentration at which bicadinanes begin to appear in the commonly published m/z 191 and 217 mass chromatograms (generated by selected ion GCMS as opposed to the MRM-GCMS method used here).

Differential preservation and/or maturation of the bicadinane and hopane precursors is a third possible reason for the wide variation in the bicadinane/hopane ratio. Bicadinanes are secondary reaction products formed during thermal destruction of polycadinene resins and are not formed in the laboratory at temperatures below 300 °C (Murray et al., 1994a; van Aarssen et al. 1991b). However, the studies of Pearson and Alam (1993)

indicated that temperatures as low as 90 °C could produce bicadinanes during natural catagenesis. Recently, Stout (1995) suggested a vitrinite reflectance as low as 0.35 % R_o for bicadinane formation, a value well below the accepted threshold for petroleum generation (R_o~ 0.6, Peters and Moldowan, 1993; Tissot and Welte, 1984). This raises the possibility that sediments immature for oil generation could nevertheless release bicadinanes and that these could then be entrained by an oil migrating from more mature regions.

Further work is needed to establish the cause of the wide variation in bicadinane/hopane ratio and hence begin to use this parameter in a more predictive manner. One approach to evaluating the influence of maturity on the bicadinane concentration is to examine it's concommitant influence on the distribution of bicadinane isomers. This is taken up in chapter five.

3.4.3 The n-Alkane isotope composition of the oils in relation to source-rock depositional environment

For most of the oil samples, the n-alkane fraction was found to be 0.5-2.0 ‰ depleted in ^{13}C with respect to the bulk saturates (Fig. 3.7) and, by implication, the branched and cyclic compounds. This value is comparable with the 1.5 ‰ depletion expected for n-alkyl with respect to polyisoprenoid lipids in biota (Hayes et al., 1990 and references therein) due to differences in isotope fractionation along the acetogenic and isoprenoid synthetic pathways. The larger difference observed for LAC 1 (2.6 ‰) may be due to the presence of the isotopically heavy botryococcane and related isoprenoids in the bulk saturates for this oil (Fig. 3.8). Similarly, the relatively large difference between the bulk saturate and n-alkane isotope values for oils FD 12 and FD 3 may be due (Smith et al., 1982) to the high concentration of isotopically heavy, resin derived compounds in these oils (e.g., bicadinanes, Fig. 3.4). For the two SAL oils from the Uinta Basin, one MC oil from the North Palawan Basin and one FD oil from the Tarakan Basin, the n-alkane fraction is isotopically heavier than the branched/cyclics. The

relative ^{13}C depletion of branched/cyclic compounds (such as the isoprenoids) in saline lacustrine oils and sediments may be related to a large cyanobacterial contribution to the kerogen (Collister et al., 1992).

The tendency for individual n-alkanes in fluvio-deltaic oils to become isotopically lighter with increasing chain length (Fig. 3.9) has been noted previously in respect of oils from South Texas (Bjorøy et al., 1991), Taiwan (Dzou and Hughes, 1993), Indonesia and Australia (Wilhelms et al., 1994). It has also been seen for pyrolysates of a Jurassic coal (Bjorøy et al., 1992). Nevertheless, this trend has not previously been recognised as characteristic of FD oils, and little attempt has been made to explain it in terms of the nature of the source. However, Chung et al. (1994) did consider the influence of depositional setting when discussing the results of a different but conceptually similar experiment. These workers attributed the trend towards isotopically lighter values for C_5 to C_{17} distillation fractions of deltaic oils to a) increased thermal cracking/kinetic isotope effect due to late expulsion and b) the smaller molecules being derived from isotopically heavier plant constituents (based on Smith et al., 1982). These explanations are reasonable for the low boiling range compounds studied by Chung et al. (1994) and for whole oil fractions containing both n-alkanes and branched/cyclic compounds. However, they cannot explain the similar trend observed for individual C_{12}-C_{32} n-alkanes. Kinetic isotope effects during oil to gas cracking are expected to cause an enrichment of ^{13}C in a whole oil with respect to the evolved gas (Clayton, 1991) but, below a level of maturity equivalent to 50 % cracking, the enrichment should be no more than 1.5 ‰ and the differential effect over the C_{12}-C_{34} range considerably less (Silverman, 1967). These predictions are confirmed by the results of artificial maturation experiments showing no major change in the n-alkane isotope profile for pyrolysis temperatures below 350 °C, and then only for oils derived from Type II organic matter (Bjorøy et al., 1992). Clayton and Bjorøy (1994) showed that individual n-alkanes become isotopically heavier with increasing maturity of North Sea (UK) oils but the magnitude of the change is less than 2 ‰ and there is no differential effect on n-alkanes in the C_{12}-C_{32} range. Dzou

and Hughes (1993) attributed changes in the isotope composition of fluvio-deltiac oils and condensates to the phenomenon of evaporative fractionation. However, while evaporative fractionation, like increasing maturity, can change the relative *abundance* of n-alkanes in an oil (and through this the isotope ratio of the bulk saturates) it cannot significantly affect the *isotope ratio of individual n-alkanes*. This is confirmed by the results of Dzou and Hughes (1993) which show differences of less than 0.5 ‰ between the δ values of C_{12} - C_{14} n-alkanes in an evaporatively fractionated oil and it's daughter condensate. Such a small difference is barely within the precision of the technique (Bakel et al., 1994).

As discussed above, and in view of the exclusion of very high maturity oils from the sample set (it includes no condensates) cracking and other secondary processes cannot have significantly affected the n-alkane isotope profiles. However, both the overall isotopic composition and n-alkane isotope profiles of low maturity oils can vary due to incomplete kerogen conversion. Boreham et al. (1994) and Collister et al. (1992) both observed changes in the shape and magnitude of n-alkane isotope profiles during artificial maturation of lacustrine kerogens, with the greatest differences occurring at low pyrolysis temperatures. Revill et al. (1994) observed a similar trend in the n-alkane isotope values with increasing pyrolysis temperature for a *Tasmanites sp.* dominated kerogen. For the lacustrine kerogens, the changes were attributed to progressive dilution of free lipids with the products of catagenesis, and in one case (Boreham et al., 1994), to the differential release of n-alkanes from *Pediastrum* and *Botryococcus* algaenans. Assuming that most of the oils used for the present study were generated within the conventional oil window, incomplete kerogen conversion should not have greatly influenced the n-alkane isotope profiles. This possibility cannot be entirely ruled out however.

The data in Fig. 3.9 suggest that source matter type and/or depositional environment are the main factors determining the shape of the n-alkane isotope profiles. In particular, negatively sloping curves occur consistently

only for FD and TR oils, suggesting that it is the abundance of land plant matter in the source which is responsible for this feature. Notwithstanding a minor algal contribution to the source of some FD oils, the n-alkanes must arise mainly from higher plants, either directly or via bacterial reworking of the primary biomass. Cutin and suberin polyesters are a possible source of both short and long-chain alkanes but especially those with 15 and 17 carbon atoms (de Leeuw and Largeau, 1993). Bacteria generate mainly short alkanes (C_{12}-C_{22}), possibly by decarboxylation of n-alkanoic acids (Lichtfouse and Collister, 1992). The resistant biopolymers found in leaf cuticles can yield both long and short chain alkanes depending on maturity (Tegelaar et al., 1989) and it is possible to explain the complete n-alkane abundance profile an FD oil in terms of the catagenesis of cutans and possibly suberans (de Leeuw and Largeau, 1993; Tegelaar et al., 1989). However, derivation of the n-alkanes from a single precursor should not yield an isotopic difference between long and short chain alkanes, as is observed for the FD oils. In support of this contention, Eglinton (1994) showed that n-alkanes derived from the cutan of *Agave americana* were isotopically uniform over the C_{13}-C_{32} range. Some plants using the crassulacean (CAM) carbon fixation pathway apparently do produce n-alkanes with an isotopic distribution similar to that observed for the FD oils, although most do not (Collister et al., 1994). Bacterial and perhaps fungal reworking of the higher plant biomass is therefore considered the most likely explanation for the characteristic isotope profiles of FD oils. It is accepted that bacterial biomass is more important in terrestrial than in marine systems and this is also evident from the higher hopane/sterane ratios for the FD versus MD and MC oils (Fig. 3.4). Based on the work of De Niro and Epstein (1978) and Coffin et al. (1990), each stage of bacterial heterotrophy results in an increase of 1 - 2 ‰ in $\delta^{13}C$. Thus, a difference of 2 - 4‰ magnitude between the $\delta^{13}C$ values of short and long chain alkanes is reasonable if the latter are directly inherited from plant waxes and biopolymer and the former arise from bacterial reworking of such materials.

Katz (1994) has argued that a subsidiary algal contribution is an important influence on the source quality of fluvio-deltaic sequences. Hence any indication of this in the n-alkane profile would be significant. However, a comparison of the data in Figs. 3.4 and 3.9 shows no discernible correlation between the overall shape or position of the n-alkane profile and biomarker indications of algal input. Nevertheless, five of the seven oils containing more than 10% C_{27} steranes do show a small ^{13}C enrichment for n-C_{17} with respect to the surrounding n-alkanes (Fig. 3.9). A plot of the magnitude of this "anomaly" against % (C_{27}+ C_{30}) steranes separates the FD oils into two main groups and two outliers (Fig. 3.10). The reason for this association of algal-derived steranes and and a small $\delta^{13}C$ enrichment in n-C_{17} is not clear, although it is noteworthy that n-heptadecane is the most abundant hydrocarbon in marine phytoplankton (Saliot, 1981 and references therein). Hence it is possible that n-heptadecane inherited directly from marine algae adds to that derived from bacterial reworking and alters the nC_{17} isotope composition for the marine influenced FD oils. Another possibility is that an unidentified co-elutant has affected the nC_{17} value for some oils and that this co-elutant is in some way associated with the higher concentration of C_{27} and C_{30} steranes. Although no co-eluting species could be recognised in mass spectra recorded across the peak, a low concentration co-elutant with a markedly different isotope composition could still cause the anomaly observed.

Of the three lacustrine oils, only LAC 1 shows a significant ^{13}C depletion for the longer chain alkanes. However, a minor terrestrial contribution to the source of LAC 2 may be indicated by the slightly ^{13}C depleted values for the odd chain-length waxy hydrocarbons compared with their even numbered counterparts. There is little doubt that resistant algaenan polymers are the primary source of n-alkanes in these oils (Boreham et al., 1994; de Leeuw and Largeau, 1993) and the relative abundance of Pediastrum and Botryococcus algae is probably the main control on their isotope composition (Boreham et al.,1994; Williams et al., 1992a). A subsidiary higher plant input is nevertheless evident from the biomarker data (Fig. 3.4).

All of the alkanes in the SAL oils are depleted in ^{13}C relative to those in the other oils, probably because of the contribution from cyanobacteria to the source (Collister et al., 1992). In fact, the n-alkanes in SAL 2 are more ^{13}C depleted than their counterparts in the well-known saline lacustrine facies of the Green River Shale (Bjorøy et al., 1992; Collister et al.,1992).
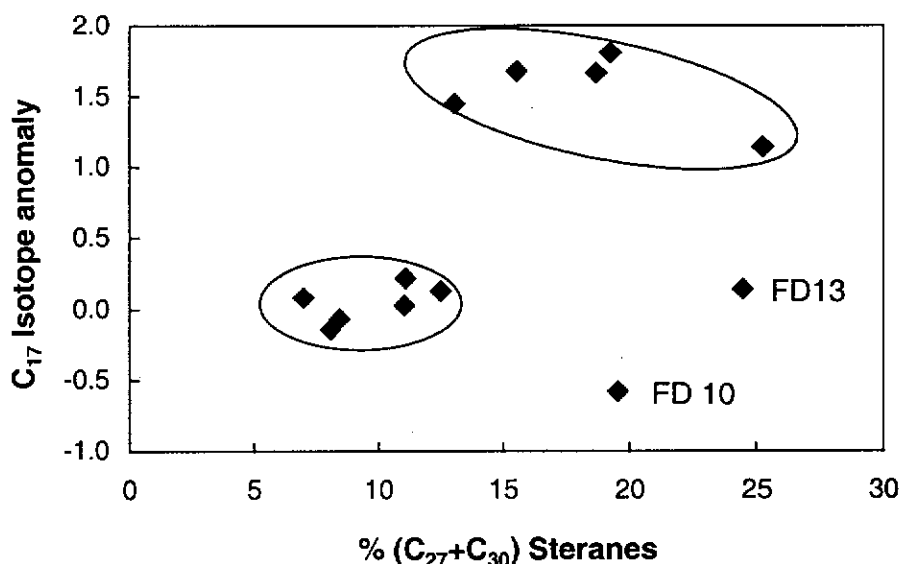
Figure 3.13   Plot of C_{17} isotope "anomaly" (‰ vs. PDB) vs the sum of % C_{27} and C_{30} desmethyl steranes for FD oils. Method of calculation of the anomaly and the sterane sum is described in Table 3.4.

For the marine deltaic (MD) and marine carbonate (MC) oils there is no simple relationship between the biomarker indications of terrestrial influence and the shape of the isotope profiles. For example, of the profiles for the marine deltaic oils, MD 1 slopes up approximately 3 ‰ from low to high carbon number, MD 2 is flat across the range and MD 3 slopes sharply down towards lighter values for the waxy n-alkanes. All three oils show biomarker evidence of a terrestrial contribution although MD 2 is probably derived from a Cretaceous, rather than Tertiary source rock and has only traces of oleanane (Murray et al., 1994b). The profile obtained for MD 1 is typical of those obtained by other workers for marine oils (Bjorøy et al., 1991; Trinidade and Brassell, 1993; Chung et al., 1994) and, despite the relatively

high abundance of oleanane in this oil (Fig. 3.4), shows little contribution from ^{13}C depleted plant biomass. Similarly, the marine carbonate (MC) oils from the North Palawan Basin, have an unusually heavy isotopic composition - heavier in fact than all 621 marine oils include in the global set studied by Chung et al. (1992). Hence, any contribution from ^{13}C depleted plant lipids should be especially apparent in the isotope profiles of these oils Yet, as shown in Fig. 3.9, the isotope composition of the n-alkanes is remarkably uniform and shows only minor ^{13}C depletion in the C_{26}-C_{31} region. Since these oils have oleanane/hopane ratios as high as many of fluvio-deltaic oils it is clear that this parameter exaggerates higher plant contribution to the marine oils.

The n-alkane profiles sometimes allow source and environmental effects to be differentiated. For example, the Octon-1 oil (MC 4) has the same flat isotope profile as others from the North Palawan Basin but is 4 ‰ lighter overall. Although this general ^{13}C depletion would be equally apparent from isotope data for the saturate fraction or whole oil, it would be natural in that case to attribute the difference to an increased contribution from land-plant organic matter. By contrast, the CSIA data show the depletion in ^{13}C to be uniform across the n-alkane range, implying a change in depositional conditions (e.g., in availability or $\delta^{13}C$ value of bicarbonate) rather than in the marine/terrestrial source content.

3.4.4 The n-alkane isotope composition of Ancient sediments containing land-plant organic matter

As discussed above, the primary control on the shape of the n-alkane profile of an oil appears to be the type of primary source matter and the degree of bacterial reworking. In particular, oils derived from coals and carbonaceous shales in the FD setting invariably give negatively sloping profiles. Direct measurement of the n-alkane isotope profiles for sediments of this type from the Buller and South Sumatra Basins confirm this trend towards more

negative $\delta^{13}C$ values with increasing chain length. Furthermore, factors other than source matter type appear to have little influence on either the slope or the absolute position of the n-alkane isotope profile. Although organic matter type and maturity are essentially constant throughout the 10m thick Buller seam, marked changes in biomarker ratios associated with variation in peat biochemistry during early diagenesis occur (see chapter six). This variation is clearly not associated with major changes in the n-alkane isotope profile. Similarly, although the South Sumatra Basin sediments cover a wide range of maturities, depositional environment and lithologies and represent several million years of deposition, the only significant change in the n-alkane isotope profile is associated with a change in the proportion of marine and terrestrial organic matter (see Fig. 3.12 vs. the biomarker data and n-alkane abundance data presented in chapter five). The relative ^{13}C enrichment of the shorter chain n-alkanes in this sample probably results from the mixed marine/land-plant input and is further evidence of the pre-eminent role of source matter type in setting the shape of the n-alkane isotope profile. Unfortunately, because of their low relative abundance, no data could be obtained for the n-alkanes below $n\text{-}C_{18}$ in most of the South Sumatra Basin samples. Thus it was not possible to test for the presence of an nC_{17} isotope anomaly.

3.4.5   Influence of plant type (conifer vs. angiosperm) on the n-alkane isotope profile

As discussed in chapter one, there is a fundamental difference in the way conifers and angiosperms assimilate carbon and in the degree to which they discriminate against the heavy isotope. Hence, all other factors being equal, the n-alkanes in oils derived from coniferous organic matter should be isotopically heavier than those in oils derived from angiosperms. This is a difficult hypothesis to test, however, because it is not easy to find a set of oils derived from conifer/angiosperm organics where "all other factors" (principally age and degree of bacterial reworking of the source matter) are

equal. Certainly, the oils analysed for the main part cannot be used to test this hypthothesis because only one (Maui, FD 5) has a significant conifer component. It is possible however to make a reasonable comparison between oils of the Taranaki Basin (NZ) and the Gippsland Basin (Australia). These two basins were formed at approximately the same time (late Cretaceous-Tertiary) at the same paleolatitude, and under similar climatic regimes. The source matter for the Gippsland oils is mainly derived from conifers (esp. Araucarians, Philp et al., 1981; Shanmugam, 1985) while in the Taranaki Basin there is a gradation from mixed conifer/angiosperm sourced oils in the south-west to angiosperm derived oils in the north-east (Killops et al., 1994b). The Maui oil (FD 5) is representative of the former class while McKee (FD 4) is typical of the latter.

The data, presented in Fig. 3.10 are fully consistent with the notion of conifer material yielding isotopically heavier n-alkanes. That is, the most ^{13}C depleted n-alkanes are found in the angiosperm derived oils, the most ^{13}C enriched n-alkanes in the conifer-derived oils and intermediate values are obtained for n-alkanes in an oil of mixed conifer-angiosperm origin. In fact, the shape of the profile for the mixed source oil may indicate that the shorter chain n-alkanes arise from conifers and the longer chain compounds from angiosperms. Such a situation could arise, for example, where a thick section of Cretaceous (conifer dominated) and overlying Tertiary (angiosperm dominated) sediments was progressively buried: the deeper and more mature Cretaceous section could in that case inject the reservoir with a distribution of n-alkanes skewed towards the molecularly "light" but isotopically "heavy" compounds.

Further evidence for an isotopic difference between conifer and angiosperm derived oils is presented in chapter four.

3.5 Conclusions

This study has shown that biomarker parameters such as oleanane/hopane ratio and bicadinane/hopane ratio provide only a crude measure of the degree of terrigenous influence on the source of an oil. In particular, a comparison between biomarker and n-alkane isotope profiles for marine oils suggests that the latter provide a more realistic indication of the scale of the terrestrial contribution.

Both oleananes and bicadinanes arise from the presence of angiosperms in the paleoflora and so provide a useful control on the age of the source beds for a given oil. However, the source of the bicadinanes is more specific than that of oleanane, leading to greater variability in their abundance and possibly also to more precise age control within the Tertiary of Southeast Asia. As predicted by others, minor amounts of bicadinanes have been shown to occur in oils from outside the paleogeographic range of the dipterocarps, confirming the role of other resinous angiosperms in their production. The presence of a suite of oleanane related triterpanes may indicate locally derived, as opposed to fluvially transported and redeposited angiosperm debris in the source rock.

Biomarker evidence for an algal contribution to the source of FD oils is tenuous and cannot be used alone to distinguish between, e.g., paralic and flood-plain depositional settings. However, negatively sloping n-alkane isotope profiles appear to be characteristic of oils generated from higher plant matter, with marine oils more commonly showing a flat or positively sloping profile. Furthermore, a slight isotopic anomaly at n-C_{17} correlates with the concentration of algal-related steranes in FD oils and may be an indication of a subsidiary marine-algal influence on their source. Source matter type is clearly the primary factor determining the shape of the n-alkane isotope profile, at least in the C_{12}-C_{34} range. Although such profiles are not sufficiently distinctive to be used in isolation, they do allow a more confident interpretation of the biomarker data and they are less subject to

non-source influences. They may be particularly useful when there is doubt as to whether trace biomarker components truly reflect the character of the bulk oil and its source.

Differences between *n*-alkane isotope profiles for otherwise similar conifer and angiosperm derived oils support the view that these plant groups differ fundamentally in the way they discriminate against ^{13}C. Used in conjunction with biomarker data, they should be useful for both specific and general oil-oil and oil-source correlation.

CHAPTER 4: THE CARBON ISOTOPE COMPOSITION OF PLANT RESINS, RESINITES AND RESIN-DERIVED COMPOUNDS IN OILS AND SEDIMENTS

4.1 Introduction

Compounds derived from plant resins are present in many oils derived from land-plant organic matter. Bicadinanes and other compounds derived from the dammar resins of dipterocarps are abundant in most Tertiary-age oils from Southeast Asia. Tri- and tetracyclic diterpenoid hydrocarbons, such as isopimarane and phyllocladane, are major components of oils derived primarily from conifer organic matter, such as those from the Gippsland Basin, Australia (Alexander et al., 1987; Noble et al., 1985b), Beaufort-MacKenzie Basin, Canada (Snowdon, 1980) and some parts of the Taranaki Basin, New Zealand (Cook, 1988; Killops et al., 1994b).

Plant resin polymers are more thermally labile than other kerogen components (Shanmugam, 1985; Stout, 1995; Tegelaar and Noble, 1994) and considerable quantities of free hydrocarbons can be present even in the fresh resins (Stout, 1995). This means that resin compounds may be relatively abundant in low maturity sediments and oils (Snowdon, 1991; Snowdon and Powell, 1982) and could strongly affect the carbon isotope composition of the branched-cyclic fraction. Furthermore, they are highly resistant to biodegradation (chapter three, Fig. 3.6; Shanmugam, 1985) so that the molecular and carbon isotope composition of a biodegraded oil might also be determined by the resin component.

As discussed in chapter one (Fig. 1.10) resins and fossil resins (resinites) can be divided into five classes on the basis of their chemical composition (Anderson et al. 1992; Anderson 1995; Anderson and Crelling, 1995 and

references therein). However, resins falling into classes I and II are by far the most common in the geosphere. The former arise from various conifers but especially the family *Araucariacea* (*Araucaria* and *Agathis* and the newly discovered genus, *Wollemia*), while the main source of class II resins are tropical hardwoods of the family *Dipterocarpacea*. The polymeric part of class I resins consists of C_{20} labdanoid moieties while the polymer in class II resins (polycadinene) is built from C_{15} cadinene moieties. Diterpanes such as phyllocladanes, pimaranes, kauranes, beyeranes, abietanes and labdanes are commonly found in sediments and oils formed from coniferous organic matter. However, whether these compounds are derived primarily from bleed (heartwood) resins or from precursors found in leaf-resins is not yet clear. Certainly, tri- and tetracyclic diterpenoids are not a major part of the polymeric structure of most class I resins (van Aarssen et al., 1991a; Anderson et al., 1992) and their concentration as free hydrocarbons in mature resinites is low (K.B. Anderson, pers.comm).

Prior to this study, very little information on the carbon isotope composition of plant resins was available. Smith et al. (1982) reported a value of -24.7 ‰ for whole resinite (probably class I) in a Victorian brown coal and - 26.9 ‰ for the insoluble residue. Horsfield et al. (1988) found an approximately linear relationship between $\delta^{13}C$ of aromatics in the bitumen and resinite+fluorescing vitrinite content of coals from the Tertiary Talang Akar Fm. (Indonesia). Although no direct measurements of $\delta^{13}C$ for resinite were made, extrapolation of the presented data indicates a value around - 26 ‰ for the soluble aromatics in this class II resinite material. This compares to a value of - 28.5 ‰ for a coal containing little resinitic material. During the course of the present project, Nissenbaum and Yakir (1995) and Stout (1995) have published $\delta^{13}C$ values for some gymnosperm (class I) and angiosperm (class II) resins respectively. A search of the literature found no $\delta^{13}C$ values for individual resin-derived compounds in oils. However, Schoell et al. (1994) have reported $\delta^{13}C$ values for diterpenoid hydrocarbons of probable resin origin in a Chinese brown coal.

In this study, carbon isotope compositions were determined for 34 resin and fossil heartwood resin samples and the results integrated with published values. In addition, compound specific isotope analysis was used to determine the $\delta^{13}C$ values of resin associated hydrocarbons in a sediment and three oils. Reasons for the apparently systematic differences observed between $\delta^{13}C$ values for class I and class II resins and the associated compounds in oils are discussed.

4.2 Samples

Details of the origin of the resin and resinite samples are given in Tables 4.1 and 4.2 respectively. Classification of the samples as class I or class II is based on the botanical origin with confirmation by either off-line or on-line pyrolysis-GCMS (as per Murray et al., 1994a). Interpretation of the GCMS results was based on Anderson et al. (1992). i.e. samples which gave labdatriene hydrocarbons, acids and alcohols on pyrolysis were confirmed as "class I" resins and those which gave cadinoid and bicadinoid compounds as "class II" resins). No attempt was made to assign the class I samples to the sub-classes 1a, b and c defined by Anderson et al. (1992) although some inferences can be made from the botanical origin. For example all those from *Araucaria* and *Agathis* species would likely be class 1b resins. Fresh resins from conifers growing in the Sydney botanic gardens were collected in December 1995. All were taken from isolated trees so as to avoid effects due to recycling of ground-litter derived CO_2. Fresh resins from dipterocarp trees (*Shorea, Drybanolops, Vatica*) and from the Araucarian conifer *Agathis borneensis* were collected in the Belalong Forest research station, Temburong, Brunei. One further sample of dipterocarp resin was collected from a recently felled tree (*Shorea albida*) in the Seria peat swamp, Brunei. Resin samples were collected from the trunk, either at the base or at heights up to 40 m from the ground.

Table 4.1   Carbon isotope composition of Class I and Class II plant resins.

Species	Location	$\delta^{13}C$ (‰)	Source and/or reference
Class I			
Wollemia nobilis	Wollemi National Park, Australia	-27.7	This study
Araucaria cunnighamii	Sydney Botanic Gardens, Australia	-26.3	This study
Araucaria cunnighamii	Sydney Botanic Gardens, Australia	-27.1	This study
Araucaria hunsteinii	Sydney Botanic Gardens, Australia	-24.1	This study
Araucaria bidwillii	Sydney Botanic Gardens, Australia	-22.9	This study
Araucaria heterophylla	Brighton Le Sands, NSW, Australia	-27.2	This study
Araucaria sp.	Israel	-23.0	Nissenbaum and Yakir (1995)
Agathis mooreii	Sydney Botanic Gardens, Australia	-24.5	This study
Agathis borneensis	Temburong, Brunei, Borneo	-26.3	This study
Agathis australis (Kauri)	New Zealand	-24.9	Murray et al. (1994a)
Cedrus deodara	Sydney Botanic Gardens, Australia	-25.7	This study
Dacrycarpus dacrydioides	Manutuke, Nr. Gisborne, NZ	-27.1	This study
Dacrydium cupressinum	Makaretu Stm., NZ	-25.6	This study
Pinus roxburghii	Sydney Botanic Gardens, Australia	-26.5	This study
Pinus radiata	Mt. Stromlo, Canberra, Australia	-27.5	This study
Pinus radiata	Mt. Stromlo, Canberra, Australia	-26.4	This study
Pinacea sp.	Israel	-25.7	Nissenbaum and Yakir (1995)
	Mean	**-25.8**	
	Standard Deviation	**1.5**	
Class II			
Shorea laevis	Temburong, Brunei, Borneo	-29.3	This study
Shorea laevis	Temburong, Brunei, Borneo	-31.6	This study
Shorea ovata	Temburong, Brunei, Borneo	-31.1	This study
Shorea leprosula	Temburong, Brunei, Borneo	-32.7	This study
Shorea leprosula	Kalimantan, Borneo	-30.8	Stout (1995)
Shorea sp.	Temburong, Brunei, Borneo	-29.9	This study
Shorea lamellata	Kalimantan, Borneo	-26.6	Stout (1995)
Shorea smithiana	Kalimantan, Borneo	-30.6	Stout (1995)
Shorea parvifolia	Kalimantan, Borneo	-31.1	Stout (1995)
Shorea ovata	Temburong, Brunei, Borneo	-31.5	This study
Shorea augustifolia	Temburong, Brunei, Borneo	-32.7	This study
Shorea ovata	Temburong, Brunei, Borneo	-30.1	This study
Shorea leprosula	Temburong, Brunei, Borneo	-30.6	This study
Shorea albida	Seria peat swamp, Brunei, Borneo	-30.8	This study
Drybanalops lanceolota	Temburong, Brunei, Borneo	-28.6	This study
Vatica micrantha	Temburong, Brunei, Borneo	-35.5	This study
Vatica umbonata	Kalimantan, Borneo	-32.3	Stout (1995)
Cotylebium sp.	Kalimantan, Borneo	-32.3	Stout (1995)
	Mean	**-31.0**	
	Standard Deviation	**1.9**	
	Difference between Class I and II	**5.2**	

Table 4.2   Carbon isotope composition of Class I and Class II resinites.

Class I	Sub-class	Age	$\delta^{13}C$ ‰	Source and/or reference
Gippsland resinite, Yallourn, Australia	1b	Tertiary	-22.8	This study and Murray et al., (1994a)
Snowline mine, Greymouth, NZ	1b	Late Cretaceous (Haumurian)	-24.2	This study
Spring Creek Rd., Greymouth, NZ	1b	Paleocene (Teurian)	-21.3	This study
Huntly Coalfield, NZ	1b	Eocene (Kaiatan)	-20.2	This study
Pirongia Mine, NZ	1b	Eocene (Kaiatan)	-21.7	This study
Giles Creek Mine, NZ	1b	Early Miocene	-23.0	This study
Heaphy Mine, Westport, NZ	1b	Middle Eocene (Bortonian)	-21.1	This study
Sicily	1b ?	Miocene	-23.5	Nissenbaum and Yakir (1995)
Baltic amber	1c	Eo-Oligocene	-24.6	Nissenbaum and Yakir (1995)
Baltic amber	1c	Eo-Oligocene	-25.6	Nissenbaum and Yakir (1995)
Manitoba, Canada	1b ?	Upper Cretaceous	-23.9	Nissenbaum and Yakir (1995)
Hermon, Israel	1b ?	Early Cretaceous	-20.2	Nissenbaum and Yakir (1995)
Philippines	1b ?	400 yrs	-24.1	Nissenbaum and Yakir (1995)
Mean			**-22.8**	
Standard Deviation			**1.7**	
Class II				
Jalan Sungei Akar, Belait Fm., Brunei		Miocene	-26.2	Murray et al. (1994a)
Coastal Resinite, South Australia		unknown (Tertiary ?)	-27.3	Murray et al. (1994a)
Coastal Resinite, South Australia		unknown (Tertiary ?)	-28.0	Murray et al. (1994a)
Talang Akar Resinite, Indonesia		Oligo-Miocene	-26.0	Horsfield et al. (1988), extrapolated
Mahakham Delta, Kalimantan, Indonesia		Miocene	-26.6	Stout (1995)
Blind Canyon, Utah, USA, resinite concentrate		Late Cretaceous	-24.1	This study
Mean			**-26.4**	
Standard Deviation			**1.3**	
Difference between Class I and II			**3.6**	

One sediment sample (AGSO #3542; Table 2.2), rich in diterpanes of the type found in Gippsland Basin oils, was also analysed. The sample is from the Gippsland Basin and is of Eocene age. Three oils (Table 4.3) were analysed by CSIA to determine $\delta^{13}C$ values for compounds derived from or

associated with resins. Based on paleobotanical and biomarker information the Dolphin, Maui and Ardjuna Basin oils are derived from conifer, mixed conifer-angiosperm (conifer dominant ?) and angiosperm floras respectively. The molecular characteristics of the Maui (FD 5) and Ardjuna Basin (FD 3) oils have been presented in chapter three.

Table 4.3   Oils analysed for the carbon isotope composition of individual resin-derived and other hydrocarbons.

Well	Basin	Type of source matter	Reference	Comments
Dolphin	Gippsland	Conifer, minor angiosperm (?)	Shanmugam, (1985)	Table 2.1, oil FD G Biodegraded, light *n*-alkanes lost
Maui-1	Taranaki	Mixed conifer and angiosperm, conifer dominant	Killops et al., (1995)	Table 2.1, oil FD-5
Confidential	Ardjuna	Angiosperm	Noble et al., (1991)	Table 2.1, oil FD-3

4.3   Analytical protocol

Branched/cyclic hydrocarbon fractions for the sediment and oils were prepared and analysed by GC-MS and GC-IRMS as described in chapter two. Diterpanes in the sediment sample were identified by comparison of their mass spectra and relative retention times with those reported in Noble et al. (1985a, 1985b) and Philp (1985).

4.4   Results and Discussion

4.4.1   The carbon isotope composition of resins and resinites

Values for the $\delta^{13}C$ ratio of fresh whole resins are presented along with values from the literature in Tables 4.1 and 4.2. These data are integrated in Fig. 4.1 to arrive at a mean and range of $\delta^{13}C$ values for resins and resinites

of each class. The reasonably wide within-class variation in $\delta^{13}C$ is expected given the many factors which can affect plant carbon isotope ratios (chapter one). This variabilty is highlighted by the fact that two *Pinus radiata* resins from the same plantation gave isotope values differing by 1.1 ‰. Despite this wide inherent variability, clear differences between conifer and angiosperm resins and between resins and resinites emerge: Firstly, class I (conifer) resins are isotopically heavier than class II (angiosperm) resins by an average 5.2 ‰. The corresponding difference for resinites is 3.6 ‰, with conifer resinites showing some of the most ^{13}C enriched values recorded for C3 plant carbon (Bocherens et al., 1994). Secondly, fresh resins of both classes are isotopically lighter than their fossil counterparts. The average difference is 3.0 ‰ for conifer resins and 4.6 ‰ for the angiosperm resins. Some possible reasons for these differences are discussed below.

4.4.2 A comparison of the carbon isotope composition of resins and resinites

Because of the widespread use of fossil fuels this century, $\delta^{13}C$ for atmospheric CO_2 is about 1.6 ‰ lower today than it was in pre-industrial times. (Farquhar and Lloyd, 1993 and references therein). Hence, to compare values for resins and resinites, 1.6 ‰ needs to be subtracted from the average difference between their $\delta^{13}C$ values. This yields resin - resinite differences of 1.4 ‰ and 3 ‰ for conifer and angiosperm resins respectively with the resins being isotopically lighter in each case.

Changes in the molecular composition of resins occur with fossilisation (Anderson, 1995; Clifford and Hatcher, 1995; Murray et al., 1994a) and the possibility of an isotope effect concurrent with these changes has to be considered. However, it is unlikely that fossilisation alters the isotope composition to the extent observed, especially for the angiosperm resins. This is because a) the basic chemical composition of resins and resinites are similar for both conifer and angiosperm resins, to the extent that they can be

recognised by pyrolysis methods regardless of the degree of diagenetic and catagenetic alteration (van Aarssen et al., 1991a, 1991b; Anderson et al., 1992 and references therein) and b) the main changes upon fossilisation are a loss of non-hydrocarbon components, a reduction in the degree of unsaturation and (for conifer resins) a loss of exomethylene groups. Of these changes, only the loss of non-hydrocarbon components is likely to cause an increase in $\delta^{13}C$. However, Stout (1995) found that the difference between $\delta^{13}C$ values for whole angiosperm resins and their hydrocarbon components ranged from +1.7 to - 1.4 ‰ with an average difference of only 0.2 ‰ (these values were calculated from the mass weighted average $\delta^{13}C$ of saturate and aromatic hydrocarbons reported by Stout (1995)). Hence, at least for these resins, loss of non-hydrocarbons upon fossilisation, would not consistently shift the $\delta^{13}C$ value in a positive direction.
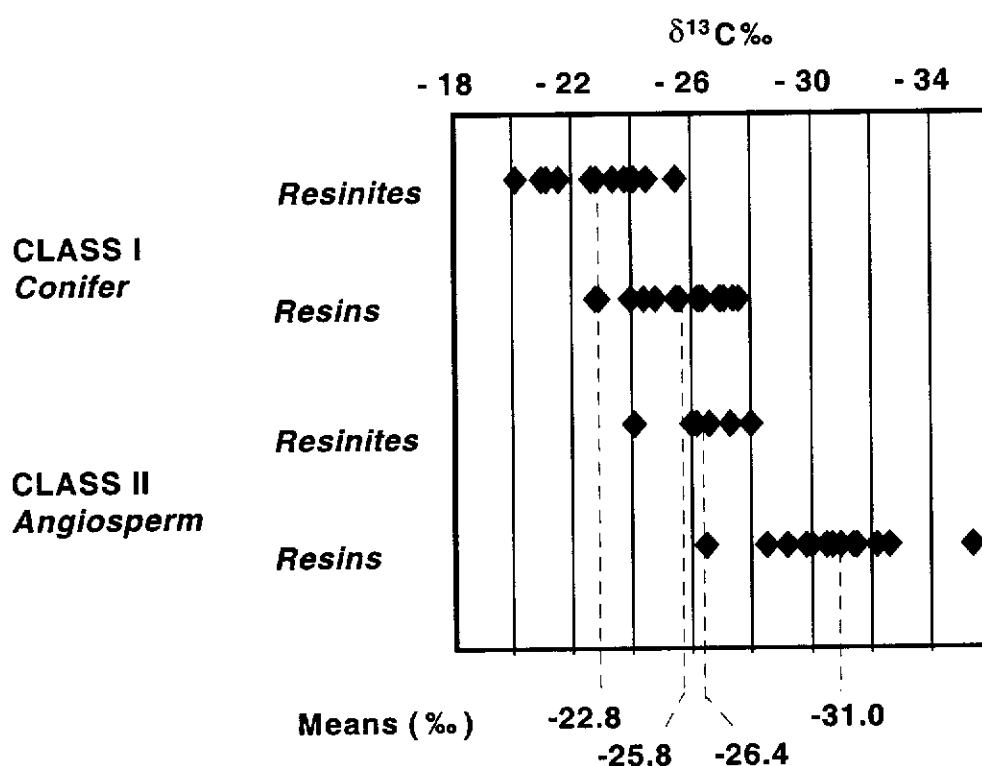
Figure 4.1   The carbon isotope composition of resins and resinites.

Since the difference between fresh and fossil samples occurs for both conifer and angiosperm resins, and is apparently of wide geographical extent, one possible reason for the difference between $\delta^{13}C$ for the recent and fossil resins is a change in atmospheric pCO_2 or $\delta^{13}CO_2$ or both between the late-Cretaceous -Tertiary and modern times. Studies of the marine carbonate and organic carbon record (e.g., Arthur et al., 1985; Popp et al., 1989; Zachos et al., 1989) suggest that such changes did occur between the Mesozoic and the present but their direction, geographic extent and magnitude are still subject to debate (Myers, 1992). Popp et al. (1989) argued that changes in $\delta^{13}C$ for marine carbon *should not* be, and in fact *are not* reflected in the record for land plant carbon. However, the evidence presented to support this view is very sparse and takes no account of differences in $\delta^{13}C$ between different plant tissues or biochemical components. The difficulty in interpreting changes in tree-ring carbon isotope ratios and other measures of atmospheric $\delta^{13}C$ during the last 10,000 years (e.g. Becker et al., 1991; Leuenberger et al., 1992; Stuiver and Braziunas, 1987) inspires little confidence that such changes can be identified over geological time. Much more data, and a set of resinites covering a more complete age spectrum are needed to assess the possibility of a temporal dependence in resinite $\delta^{13}C$.

Another possible reason for the isotopic difference between fresh and fossil resins is that environmental conditions which were conducive to fossilisation of plant resins also caused enrichment in ^{13}C. Most of the fossil resin samples were associated with deltaic or flood-plain coals and presumably some degree of ecophysiological stress preceded senescence of the swamp flora and deposition of resinite among the other coal macerals. Most stress factors, and especially the increase in groundwater salinity which would accompany transgressive drowning of a swamp, will cause an increase in $\delta^{13}C$ (Farquhar et al., 1989 and references therein). Furthermore, trees growing along the edge of watercourses in a delta might be expected to contribute more to the fossil carbon pool than those in the deeper forest. The

CO_2 respired by such trees would have a lower contribution from recycled carbon (i.e., less "canopy" effect) and so would be isotopically heavier. Again, a wider range of resinites representing different depositional environments, is needed to test these hypotheses. Among the current set, only one class II resin sample (*Shorea albida*, Table 4.1) comes from a swamp setting while all others are from dryland forest. Preliminary data for $\delta^{13}C$ of leaf waxes (Australian Geological Survey Organisation, unpublished) suggests that the tree which exuded this resin was indeed less subject to the canopy effect than others in the sample set. However, the $\delta^{13}C$ value for the resin itself does not differ significantly from the mean for all class II resins (Table 4.1).

4.4.3 A comparison of the carbon isotope composition of Class I (conifer) and Class II (angiosperm) resins

The $\delta^{13}C$ values of the conifer and angiosperm resins and resinites (Tables 4.1 and 4.2) are consistent with a fundamental difference in the way these plant groups assimilate ^{13}C. There are at least two reasons for this difference (which the data suggest has existed since at least the late Mesozoic era). Firstly, most conifers have a narrow leaf morphology and lower stomatal conductance than broad leaf species. This means that they are more water conservative and also that they assimilate CO_2 less efficiently than angiosperms where both are growing in a mixed lowland forest. Because of this, the ratio of ambient to intercellular pCO_2 (Pi/Pa, see chapter one) is lower and discrimination against the heavy isotope is reduced. Secondly, there is some evidence that conifer forests, with a more open structure than dense, tropical angiosperm forests, respire less recycled CO_2, again leading to relatively greater incorporation of ^{13}C (Broadmeadow and Griffiths, 1993 and references therein).

In keeping with the results for the resins, several studies have demonstrated a difference between $\delta^{13}C$ for modern "conifer" and "angiosperm" carbon. For

example, Stuiver and Braziunas (1987) found conifer wood to be on average 3 ‰ heavier than wood from various "deciduous" tree species. Based on several earlier studies, Lloyd and Farquhar (1994) assigned $\delta^{13}C$ values of - 23.4 ‰ (assuming $\delta^{13}C_{atm}$ = - 8 ‰) to the primary carbon of a cool/cold conifer forest biome compared with -27.6 ‰ for a cool/cold deciduous forest and - 26.4 ‰ for tropical rain forest. Marshall and Zhang (1993), again using data from several previous studies and assuming $\delta^{13}C$ atm of - 8 ‰, found an average $\delta^{13}C$ for conifer wood of -24.7 ‰. This was 3.9 ‰ heavier than the value of -28.6 ‰ given by O'Leary (1988) as the average for C3 plants generally. Saurer et al. (1995) found $\delta^{13}C$ for cellulose in Beech (ca. - 26 ‰) to be 2.5 ‰ lighter than cellulose from pines and as much as 4 ‰ lighter than that from spruce, all three species growing at the same site. From these and other studies, typical $\delta^{13}C$ values for conifer and angiosperm wood are ~ -23 and - 26 ‰ respectively. To compare these values to those for the resins, allowance needs to be made for the differences in $\delta^{13}C$ between different plant biochemicals. Isoprenoidal lipids, such as those found in resins, are characteristically depleted in ^{13}C relative to non-lipids, the magnitude of the difference varying between 2 and 6 ‰ (De Niro and Epstein, 1978; Park and Epstein, 1961; Schoell, 1984b and references therein). Using an average value of 4 ‰, yields predicted values of - 27 and - 30 ‰ for recent conifer and angiosperm resins respectively. Considering the many uncertainties in such calculations, these values agree reasonably well with the measured values of -25.8 ± 1.5 and -31.0 ± 1.9 ‰ (mean ± std. devn., Table 4.1).

4.4.4 Differences between resinites and associated coals

Further support for a fundamental difference in $\delta^{13}C$ between conifer and angiosperm carbon is found in the comparison between $\delta^{13}C$ values for resinites and associated coals from some New Zealand coal fields (Table 4.4). The class I (conifer) resinites from the Huntley coalfield and Heaphy

mine and Spring Creek mines are 4.7 ‰ to 5.6 ‰ heavier than the associated coals. Such large differences would be difficult to explain if both the resinites and their host coals arose from a conifer flora. However, the Paleocene - Eocene flora in New Zealand was dominated by angiosperms (Mildenhall, 1980) and, as discussed in chapter six, the Eocene coals of the nearby Buller coal fields are derived primarily from an angiosperm flora with only a minor contribution from gymnosperms. This gymnosperm component is however the most likely source of the resinites. A class I resinite from the snowline mine shows a $\delta^{13}C$ value closer to that of the associated coal, which is of late Cretaceous age. The parent organic matter for this coal is probably derived from conifers of the podocarp, araucaria and cypress families (Killops et al., 1995; Mildenhall, 1980). Note, however that the $\delta^{13}C$ value (-26.8 ‰) is 1 ‰ *lighter* than those of the Eocene coals and is in fact more typical of modern angiosperm derived carbon (see above).

Only one sample of a coal associated with a class II resinite was available for this study (Table 4.4). This coal of Miocene age was derived from an angiosperm flora and it's $\delta^{13}C$ value is only 0.3 ‰ less than that of the corresponding resinite. This compares with the estimated -2.5 ‰ difference between Oligo-Miocene Talang Akar Fm. coals and resinite found by Horsfield et al. (1988).

4.4.5 Individual resin-derived hydrocarbons in sediments and oils

The total ion GCMS chromatogram for a sediment from the Tuna #2 well in the Gippsland Basin is shown in Fig. 4.2. The distribution of diterpanes in the extract is similar to that seen in oils from the Gippsland Basin (Noble et al., 1995a,1995b). The sample also contains isoprenoid hydrocarbons thought to be mainly derived from the phytyl chain of land plant chlorophyll and hopanoid hydrocarbons derived both from plants (especially C_{30} diplopterol;

Pant and Rastoggi, 1979) and bacterial membrane lipids (Rohmer et al., 1992).

The most abundant diterpane, 16β(H)-phyllocladane, has a $\delta^{13}C$ value (- 23.0 ‰) close to the average value for conifer resinites (Table 4.2) whereas the plant derived isoprenoids and the hopanoids show lighter values ranging from - 25.9 to - 29.1 ‰. Among the diterpanes commonly found in oils, phyllocladane is the only compound strictly associated with gymnosperms, others having been found in angiosperms as well (albeit less frequently: Alexander et al., 1987 and references therein).

Table 4.4   Differences between the carbon isotope composition of resins and their associated coals.

Location	Age	Class	Resinite	$\delta^{13}C$ ‰ Coal	Diff.
Snowline mine, Greymouth	Late K (Haumurian)	I	-24.2	-26.8	2.6
Spring Creek Rd., Greymouth	Paleocene (Teurian)	I	-21.3	-26.9	5.6
Huntly Coalfield, NZ subunit B	Eocene (Kaiatan)	I	-20.2	-25.8	5.6
Heaphy Mine, Westport, Subunit B	Middle Eocene (Bortonian)	I	-21.1	-25.8	4.7
Brunei, Jln. Sg. Akar, Belait Fm.	Miocene	II	-26.2	-26.5	0.3

Thus the $\delta^{13}C$ value obtained may be seen as representative of the conifer carbon in the sample or at least that derived from conifer resins (leaf or heartwood). Note however that phyllocladane has also been found in Carboniferous coals (ten Haven et al., 1992a) and may be derived from primitive conifers, the *Voltziales*.

Schoell et al. (1994) reported that plant-derived hydrocarbons in a Tertiary brown coal from China could be divided into two distinct groups on the basis of their carbon isotope ratios. Diterpanes such as norpimarane and fichtelite fell into one group having an average $\delta^{13}C$ value of - 25.0 ‰ whereas compounds representative of angiosperms such as oleananes, ursanes and lupanes gave $\delta^{13}C$ values averaging - 29.0 ‰. The authors suggested that

the difference may have been due to different biosynthetic fractionation operating for leaf lipids (oleanane etc.) as opposed to "resin" constituents (norpimarane, fichtelite etc). Some support for this explanation is found in the observation that leaf tissue cellulose may be up to 4 ‰ depleted in the heavy isotope compared with the same compound in the heartwood (Leavitt and Long, 1982). However, the marked isotopic difference between the diterpane and triterpane hydrocarbons for the Chinese coal is also readily explained by their respective origins from conifer and angiosperm elements of the flora.

Compound specific and bulk carbon isotope data for two oils representing conifer and mixed angiosperm-conifer floras are shown in Figs. 4.3 and 4.4 respectively. The most abundant diterpane in the Dolphin oil is 16β(H) phyllocladane and the $\delta^{13}C$ value (-24.3 ‰) of this compound is compatible with an origin from conifer (class I) resins. Other hydrocarbons in the sample are isotopically lighter, especially phytane which may have a partial origin from methanotrophic bacteria (Brassell et al., 1985). Isopimarane is the most abundant diterpane in the Maui oil (Fig. 4.4). This compound gave a $\delta^{13}C$ value (-25.9 ‰) slightly outside the range observed for fossil conifer resins although still within two standard deviations of the mean. The slightly lighter value might indicate a partial angiosperm origin for isopimarane or an association with "leaf" rather than heartwood resins. As was the case for the Dolphin oil (Fig. 4.3), the class I resin associated compound is significantly enriched in the heavy isotope compared with other hydrocarbons. Hence, for both oils, loss of n-alkanes by biodegradation would probably cause the $\delta^{13}C$ value for the bulk saturates to increase.

Carbon isotope values for individual compounds in an oil from the Ardjuna Basin, Indonesia are shown in Fig. 4.5. This oil is of Tertiary age and the primary organic matter is derived from angiosperms including Dipterocarpaceae. The relatively light (i.e., ^{13}C depleted) value for phytane as compared to pristane is however evidence of a subsidiary contribution from methanotrophic bacteria (Brassel et al., 1985). The bicadinane isomers show

$\delta^{13}C$ values (-27.9 ‰) at the "light" end of the range for class II resinites but these resin-derived compounds are still isotopically heavier than most other hydrocarbons in the sample. Complete loss of the n-alkanes through biodegradation would therefore increase the bulk saturates $\delta^{13}C$ value but to a lesser extent than for the conifer influenced oils.

In chapter three it was noted that the n-alkane fraction for the Ardjuna Basin oil ("FD-3") was 2 ‰ depleted in ^{13}C with respect to the bulk saturates. This was somewhat more than the average degree of depletion for fluvio-deltaic oils and it was suggested that the high concentration of resin-derived hydrocarbons may have been responsible. The new data in Fig. 4.5 now show that this explanation is reasonable since the bicadinanes are among the most ^{13}C enriched compounds in the oil.
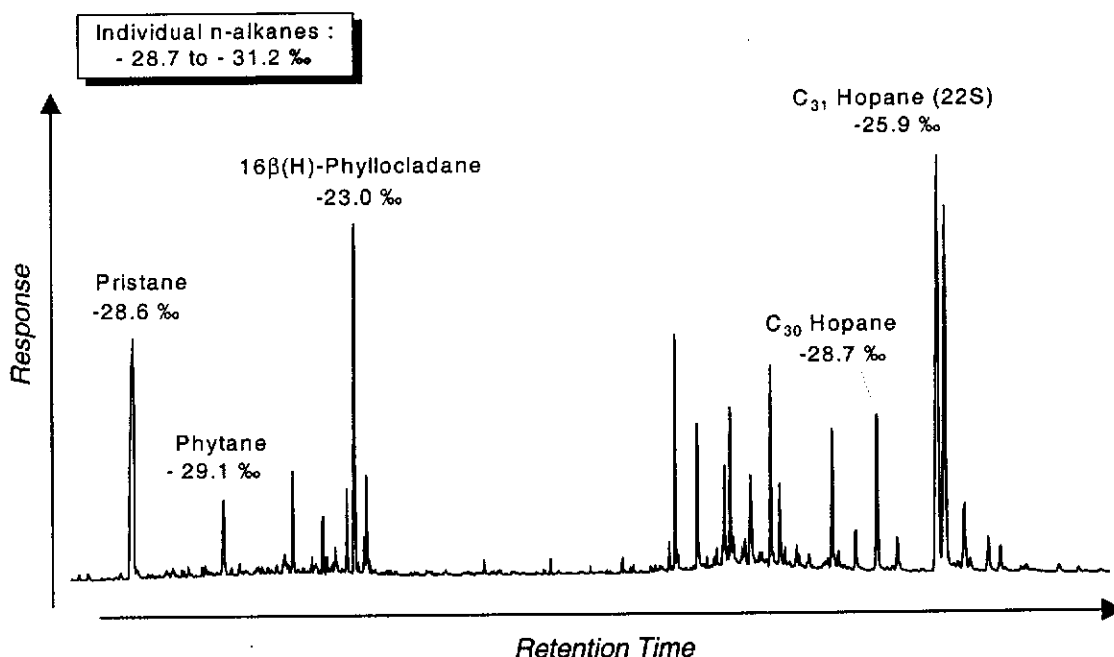
Figure 4.2   Partial GCMS total ion chromatogram of branched/cyclic hydrocarbons in a sediment from the Gippsland Basin. Annotations show the carbon isotope composition of some individual compounds as determined by GC-IRMS. Inset shows the range of $\delta^{13}C$ values for n-alkanes from the same sample.

Figure 4.3 (chart)

Pristane
-27.8 ‰

Phytane
-41.5 ‰

16β(H)-Phyllocladane
-24.3 ‰

* incompletely removed
n-alkanes

	$\delta^{13}C$	
Bulk saturates	-26.8	‰
n-alkane fraction	Biodegraded	
Indiv. n-alkanes (residual)	-26.7 to -30.3	‰

Response — *Retention Time*
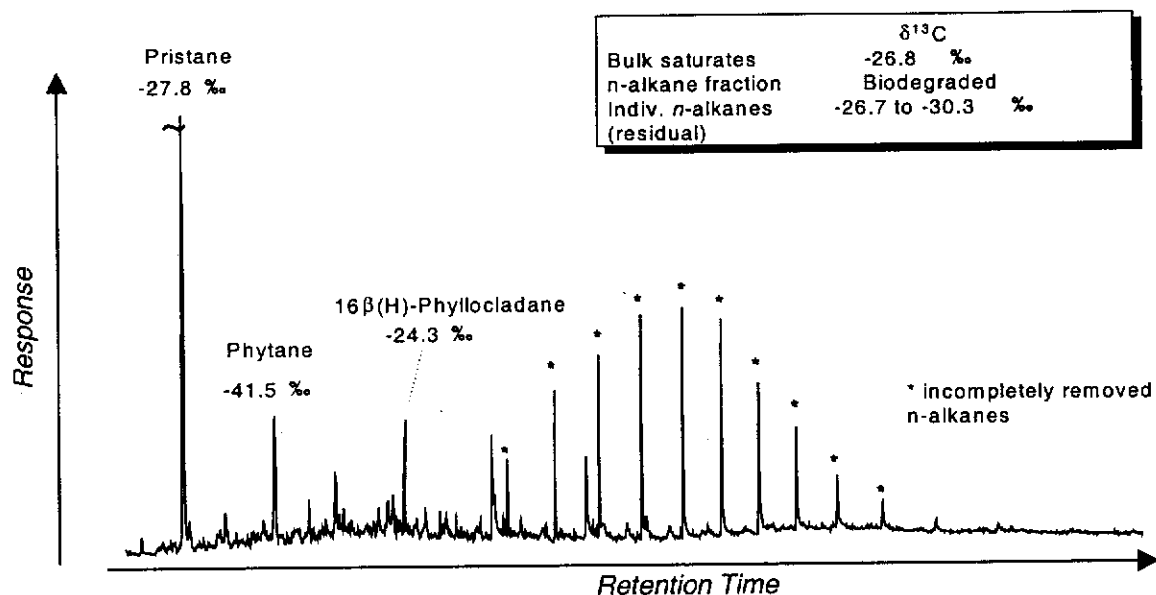
Figure 4.3   Partial GCMS chromatogram showing the carbon isotope composition of individual hydrocarbons in the Dolphin oil of the Gippsland Basin as determined by GC-IRMS.

Figure 4.4 (chart)

Isopimarane
-25.9‰

Pristane
-28.7 ‰

Phytane
-30.5 ‰

	$\delta^{13}C$	
Bulk saturates	-27.5	‰
n-alkane fraction	-28.3	‰
Indiv. n-alkanes	-25.5 to -29.9	‰

Response — *Retention Time*
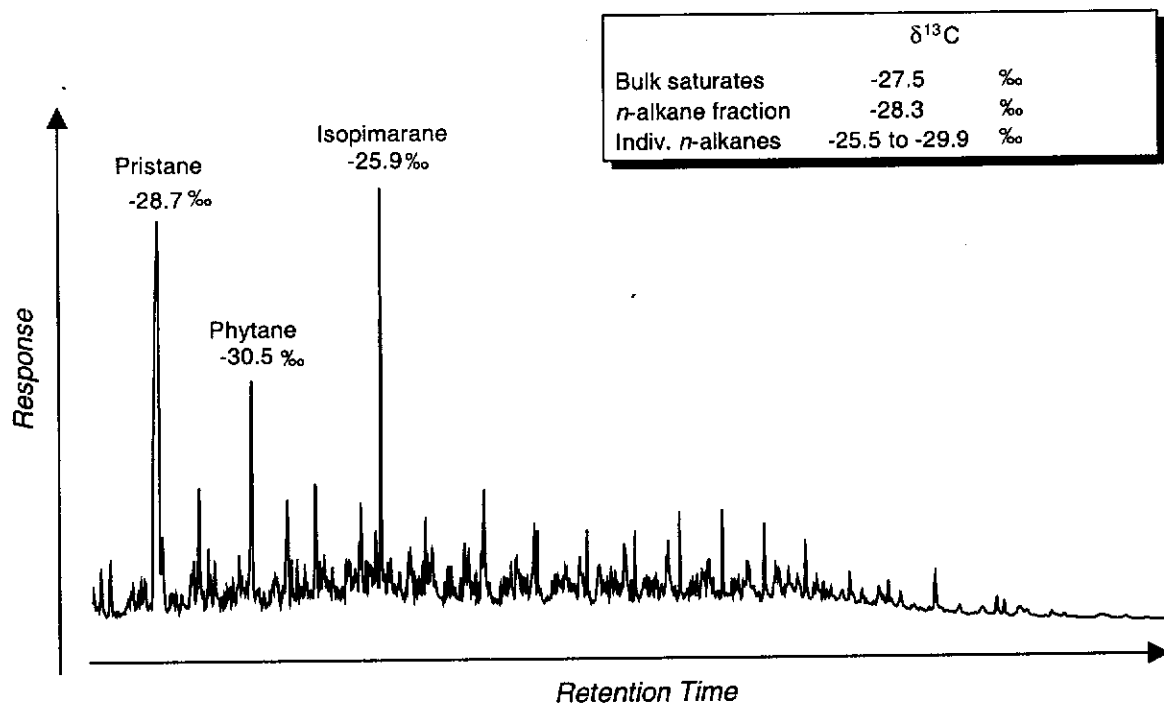
Figure 4.4   Partial GCMS chromatogram with annotation showing the carbon isotope composition of individual branched/cyclic hydrocarbons in the Maui oil, Taranaki Basin.

δ13C

Bulk saturates	-29.0	‰
n-alkane fraction	-31.0	‰
Indiv. n-alkanes	-26.6 to -33.6	‰

Pristane
-29.8 ‰

Response

T
-27.9 ‰

Bicadinanes

W
-27.9 ‰

Phytane
-33.9‰

Retention Time
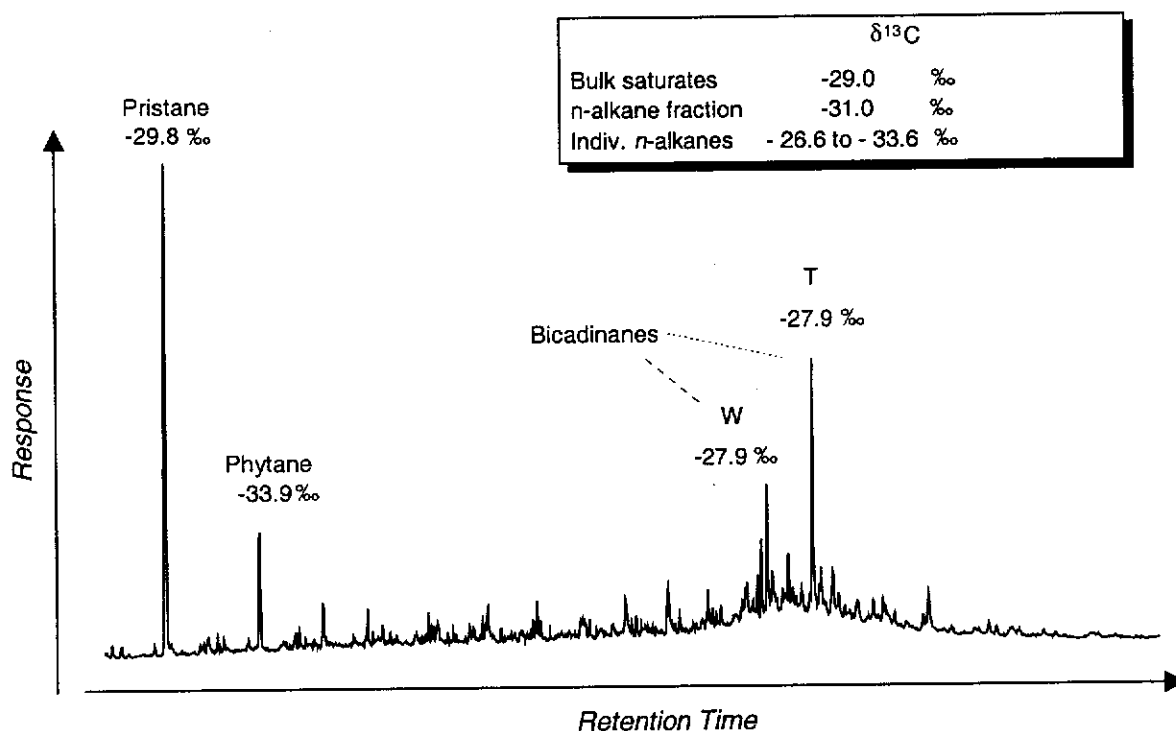
Figure 4.5 Partial GCMS chromatogram with annotation showing the carbon isotope composition of individual branched/cyclic hydrocarbons in an oil from the Ardjuna Basin, Indonesia.

4.4.6 Implications of the results for $\delta^{13}C$ of oils

As discussed above, the presence of isotopically heavy resin-derived compounds in an oil or sediment will increase the $\delta^{13}C$ value for the whole oil or bulk fractions. Furthermore, the loss during biodegradation of firstly, the isotopically light n-alkanes and, secondly, the isoprenoids, will shift the bulk isotope values towards those representative of the resin compounds. This is especially so for oils containing conifer-derived resin compounds. The very heavy $\delta^{13}C$ values for compounds associated with class I resins appear to be part of a general pattern of ^{13}C enrichment for conifer carbon with respect to that derived from angiosperms. If so, oils derived from conifer organic matter, whether or not they contain resin compounds, should show heavier isotope values than those derived from angiosperms.

A plot of saturate fraction $\delta^{13}C$ values against oleanane/hopane ratio for oils from the Gippsland and Taranaki Basins is shown in Fig. 4.6. Many

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similarities between these two basins have been noted including source age and general type, depositional environment, paleolatitude and paleoclimate (Killops et al., 1994b, 1995; Shanmugam, 1985). However, the Gippsland oils are considered to have come mainly from sediments containing coniferous organic matter whereas those of the Taranaki Basin show varying degrees of angiosperm influence. As discussed later (chapter six), caution must be exercised in using oleanane/hopane as an indicator of the degree of angiosperm influence, as oleanane abundance is sensitive to conditions during early diagenesis. In this case, however, the oils come from basically similar depositional settings and oleanane/hopane provides a rough guide to the conifer-angiosperm source balance. There is little doubt, for example, that the Maui and McKee oils are respectively among the most conifer and angiosperm influenced oils in the Taranaki Basin (Killops et al., 1995). The plot confirms that the most conifer influenced oils have the heaviest carbon isotope values for the saturate fraction, and that, generally speaking, higher oleanane/hopane ratios are associated with more ^{13}C depleted oils. Individual n-alkanes in the Gippsland oils are relatively enriched in ^{13}C as compared with those in angiosperm derived oils (Fig. 3.10, chapter three).

* Biodegraded oils excluded
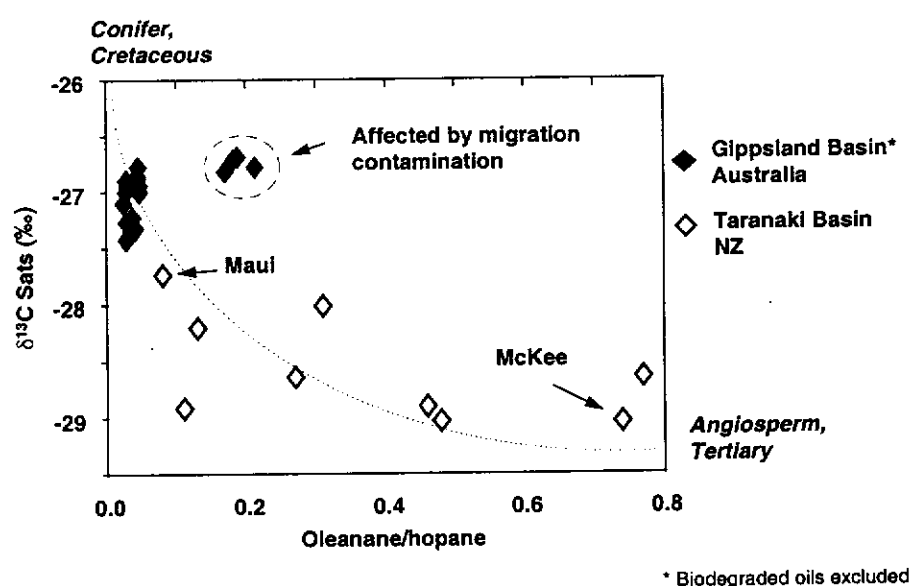
Figure 4.6   Crossplot of $\delta^{13}C_{sats}$ against oleanane/hopane for oils of the Gippsland and Taranaki Basins. Data courtesy of Geomark Research Inc. (C. Schiefelbein, pers.comm.).

The value of a crossplot of two variables responding to a common influence is that anomalies can be identified. This is seen in Fig. 4.6 where a group of Gippsland oils (circled) plots away from the trend. All of these oils have entrained oleanane during migration through coaly sediments and also show the characteristic enrichment in the C_{31} homohopanes (especially the R epimer) recorded by Philp and Gilbert (1982) for an oil from Turrum-2. The crossplot helps to confirm that the presence of oleanane in these oils is due to migration contamination, as opposed to co-sourcing from Tertiary sediments containing angiosperm matter.

4.5 Conclusions

Conifer resins and their catagenetic products in oils and sediments are isotopically heavy compared with angiosperm resins and compounds derived from them. This difference has existed since at least the late Mesozoic and is probably a result of fundamental differences in the way conifers and angiosperms assimilate carbon. Modern plant resins are isotopically light compared with their fossil counterparts. The reasons for this are not clear but may include secular change in the composition and partial pressure of atmospheric CO_2 and/or ecological stress and reduced canopy effect for trees more prone to fossilisation. Resin derived compounds in oils and sediments, especially those associated with conifers, are isotopically heavier than other hydrocarbons. Since resin compounds are also more resistant to biodegradation, degradative loss of the n-alkanes and isoprenoids will cause the bulk $\delta^{13}C$ values of oils derived from resinous matter to rise more than is the case for non-resin rich oils.

The isotopic difference between conifer and angiosperm carbon, manifested here in the results for resins, also has consequences for the bulk carbon isotope composition of oils formed from land-plant matter. Oils formed from

conifer material appear to be isotopically heavier overall than those derived from angiosperms. However, a larger data set is needed to confirm this observation and to distinguish it from secular change in the $\delta^{13}C$ of fossil carbon.

CHAPTER 5:   BICADINANES AND RELATED COMPOUNDS AS MATURITY INDICATORS FOR OILS AND SEDIMENTS

5.1   Introduction

Large volumes of oil have been generated by deltaic petroleum systems in Southeast Asia, Australia and New Zealand. Estimating the maturity of deltaic oils can be difficult for several reasons: Firstly, some biomarker compounds used to estimate maturity, such as the epimeric steroids, are present at low concentration in oils formed from terrigenous matter. Secondly, the wide variation in sediment Eh/pH across a delta can profoundly affect reactions occurring during early diagenesis (Dahl et al., 1993; Moldowan et al., 1986; ten Haven et al., 1986), causing changes in "maturity" indicators which are unrelated to thermal stress. Finally, for reasons which are not yet clear, Tertiary-age oils often have lower and more variable sterane and triterpane maturities than those from older source rocks (Grantham, 1986).

During pyrolysis experiments with dammar resin (Murray et al., 1994a), it was noted that the distribution of bicadinanes was sensitive to heating time. In this chapter, new maturity indices based on these changes, and on others which occur in the distribution of diaromatic secobicadinanes, diaromatic tricadinanes and cadalenes (Alexander et al., 1994; Sosrowidjojo et al., 1993,1994) are proposed and/or tested. Almost all the Tertiary oils of Southeast Asia contain these and other compounds formed during catagenetic dissociation of polycadinene - a major constituent of resins exuded by some tropical angiosperms (van Aarssen et al., 1990a, 1992a, 1994; Murray et al., 1994a). Since polycadinene does not break down until subsurface temperatures reach ca. 80 °C (Tegelaar and Noble, 1993), most microbial activity should have ceased before bicadinanes and related

compounds become available. Hence, polycadinene-related maturity indices may be less prone to biochemical and chemical effects during early diagenesis (hereafter referred to as "diagenetic effects") than those based on steranes and hopanes. Furthermore, since migration contamination is interpreted to have affected source characterisation of several Tertiary or Late Cretaceous fluvio-deltaic oils (Hoffmann et al., 1984; Morelos-Garcia et al., 1993; Philp and Gilbert, 1982), it is important to know whether the bicadinanes in an oil were generated at the same thermal maturity as the oil itself.

In the the first part of this chapter, new maturity indices based on the distribution of bicadinane isomers in outcrop sediments from the Philippines are described. Values for these indices and several others related to polycadinene catagenesis were also measured for cuttings from a well in the South Sumatra Basin. The results are compared with other biomarker and non-biomarker maturity indicators and with the maturity required for oil generation as predicted by kinetic modelling. In addition, values for the same indices have been measured for a set of oils from Southeast Asia, Papua New Guinea, New Zealand and Australia.

5.2   Samples

Sampling locations and basic geochemical data for the sediments and oils used in this study were presented in chapter two (Tables 2.1 and 2.2). However, for convenience, a summary of the origin of the samples (Tables 5.1 and 5.2) and some brief contextual information is given here.

The Visayan Basin (Philippines) sediments are from outcrop of the Miocene Taog, Tagnocot and Bata formations exposed on the Island of Leyte. The kerogens are of mixed lacustrine algal and land plant origin and are immature to early oil-window maturity (Murray et al., 1992; Wehner, 1989). Samples from the South Sumatra Basin are cuttings from the GK well (South

Palembang sub-basin) and a generalised stratigraphy appears in Fig. 2.1. They are from a section through the Gumai and Talang Akar formations and the depositional environment changes from marine, through shallow marine/paralic to fluvio-deltaic with increasing depth. Only the deepest samples have entered the oil window and the zone of peak oil generation is not penetrated by the GK well. The basin history is relatively simple (Sosrowidjojo et al., 1994 and references therein) and for the purposes of this study increasing depth is equated to an increasing time-temperature integral, i.e., increasing thermal stress.

Table 5.1   Geological data for sedimentary rock samples.

Depth (m)	Formation	Environment	Lithology	Ro (%)[†]
Visayan Basin, Outcrop				
Surface 1	Taog	Floodplain/Lacustrine	Shale	na
Surface 2	Taog	Floodplain/Lacustrine	Shale	na
Surface 3	Taog	Floodplain/Lacustrine	Shale	na
Surface 4	Taog	Floodplain/Lacustrine	Sltstn/Sndstn	na
Surface 5	Taog	Floodplain/Lacustrine	Shale	na
Surface 6	Taog	Floodplain/Lacustrine	Shale	na
Surface 7	Taog	Floodplain/Lacustrine	Shale	na
Surface 8	Taog	Floodplain/Lacustrine	Shale	na
Surface 9	Taog	Floodplain/Lacustrine	Shale	0.46
Surface 10	Taog	Floodplain/Lacustrine	Shale	na
Surface 11	Taog	Floodplain/Lacustrine	Shale	na
Surface 12	Taog	Floodplain/Lacustrine	Shale	na
Surface 13	Taog	Floodplain/Lacustrine	Shale	na
Surface 14	Bata	Floodplain/Lacustrine	Sltstn	na
Surface 15	Bata	Floodplain/Lacustrine	Shale	na
Surface 16	Tagnocot	Floodplain/Lacustrine	Shale	na
South Sumatra Basin, GK well				
1114	Gumai	Marine	Shale	na
1270	Gumai	Marine	Shale	0.4
1351	Gumai	Marine	Shale	0.5
1463	Talang Akar (TRM)	Shallow marine	Shale	0.6
1514	Talang Akar (TRM)	Shallow marine	Shale	na
1742	Talang Akar (TRM)	Fluvio-Deltaic	Coal	0.6
1802	Talang Akar (GRM)	Fluvio-Deltaic	Shale	0.6
1862	Talang Akar (GRM)	Fluvio-Deltaic	Coal	na
1959	Talang Akar (GRM)	Fluvio-Deltaic	Coal	na
2026	Talang Akar (GRM)	Fluvio-Deltaic	Coal	0.7
2069	Talang Akar (GRM)	Fluvio-Deltaic	Carb. Shale	na
2259	Talang Akar (GRM)	Fluvio-Deltaic	Coal	0.9
2309	Talang Akar (GRM)	Fluvio-Deltaic	Coal	0.9

TRM = Transitional member, GRM = Gritsand member, [†] Mean vitrinite reflectance ± 0.1% RSD na = not available

Polycadinene and other maturity indices were also measured for a set of 17 oils derived from rocks containing terrigenous organic matter (16 fluvio-deltaic, 1 marine carbonate) from Southeast Asia, Papua New Guinea, New Zealand and Australia (Table 5.2). The set includes two oils from offshore Brunei (FD B1 and FD B2) which were reported by Grantham (1986) to have unusually low sterane and triterpane maturities. The Gingin oil from the Perth Basin (FD P) is believed to originate from a Jurassic-age source rock (Summons et al., 1995), all others from Tertiary-age source rocks (see Table 2.1).

Table 5.2   Origin of oils analysed for polycadinene-related maturity indicators.

Number	Name	Basin	Country
FD 1	Conf.	Tarakan	Indonesia
FD 2	Conf.	Tarakan	Indonesia
FD 3	Conf.	Ardjuna	Indonesia
FD 4	M'Kee	Taranaki	New Zealand
FD 6	Conf.	Ardjuna	Indonesia
FD 9	Conf.	Ardjuna	Indonesia
FD 10	BP-OS-01	SE Luzon	Philippines
FD 11	Reina Regente	Visayan	Philippines
FD 12	Conf.	South Sumatra	Indonesia
FD 13	Lufa Seep	Papuan	P.N. Guinea
FD SSB1*	Conf.	South Sumatra	Indonesia
FD SSB2*	Conf.	South Sumatra	Indonesia
FD SSB3*	Conf.	South Sumatra	Indonesia
FD B1	Conf.	Offshore Brunei	Brunei
FD B2	Conf.	Offshore Brunei	Brunei
FD P	Gingin	Perth	Australia
MC 3	Galoc	N.Palawan	Philippines

5.3   Analytical protocol

Sediment extracts and oil samples were analysed by gas chromatography (pristane, phytane, n-alkane distribution) and gas-chromatography-mass spectrometry (cyclic biomarkers) as described in chapter two. Separate GCMS analyses of dilute and more concentrated sample aliquots were used to measure bicadinane and sterane isomer distributions respectively. This avoided a problem encountered in preliminary work with oils where distortion of the bicadinane isomer distribution occurred through overloading of the

GCMS system. Gas chromatographic data for the Visayan Basin sediments are not presented here but are given in Murray et al. (1992).

5.4   Results and Discussion

5.4.1 Effect of maturity on the isomeric distribution of bicadinanes - a preliminary study using Visayan Basin outcrop sediments

The bicadinane distributions of an immature Visayan Basin sediment, an early mature sediment and a seep oil are shown in Fig. 5.1. Also included are chromatograms for dammar resin pyrolysates generated over 120 h and 136 h at 350 °C (from Murray et al., 1994a). These data show two changes in the isomer distribution under increasing thermal stress: a reduction in the abundance of compounds T1 and R with respect to compound T, and an increase in the relative abundance of W and other cis-cis-trans isomers. Similar, although less easily measured changes occur for the methyl bicadinanes (Fig. 5.2). van Aarssen et al. (1992a, 1992b) commented on the higher relative abundance of cis-cis-trans bicadinane in oils as compared to sediments and speculated that this could be due to preferential migration. Curiale et al. (1994), working on oils from Myanmar, reported a correlation between the W/T ratio and maturity as measured by the T_s/T_m ratio. Recently, Stout (1995) has shown that the W/T ratio is probably influenced by both maturity and preferential expulsion from the source rock.

Various peak area ratios can be used to express maturity effects on the bicadinane isomer distribution. Three new "bicadinane maturity indices" or "BMI" are defined, these being: the ratio of compound T to the other trans-trans-trans isomers (BMI 1), the equivalent ratio for the methyl bicadinanes (BMI 2) and the ratio of total cis-cis-trans (cct) to total trans-trans-trans (ttt) isomers (BMI 3). The variation in these ratios against the C_{29} sterane $\alpha\alpha\alpha$ 20S/(20S+20R) ratio for the Visayan Basin samples is shown in Fig. 5.3. Also included, for purposes of comparison, are data for another common

maturity indicator, the C_{31} homohopane 22S/22R ratio. The plots show clearly that all three BMI increase with maturity as measured by the sterane epimer ratio. For BMI 2 and BMI 3 some of the scatter in the data is due to the difficulty in measuring the small peaks for the less stable isomers at high maturity. The risk of interference from co-eluting, non-bicadinane compounds is also greatest when the peaks are small, and this probably accounts for the single outlier in the plot for BMI 3.
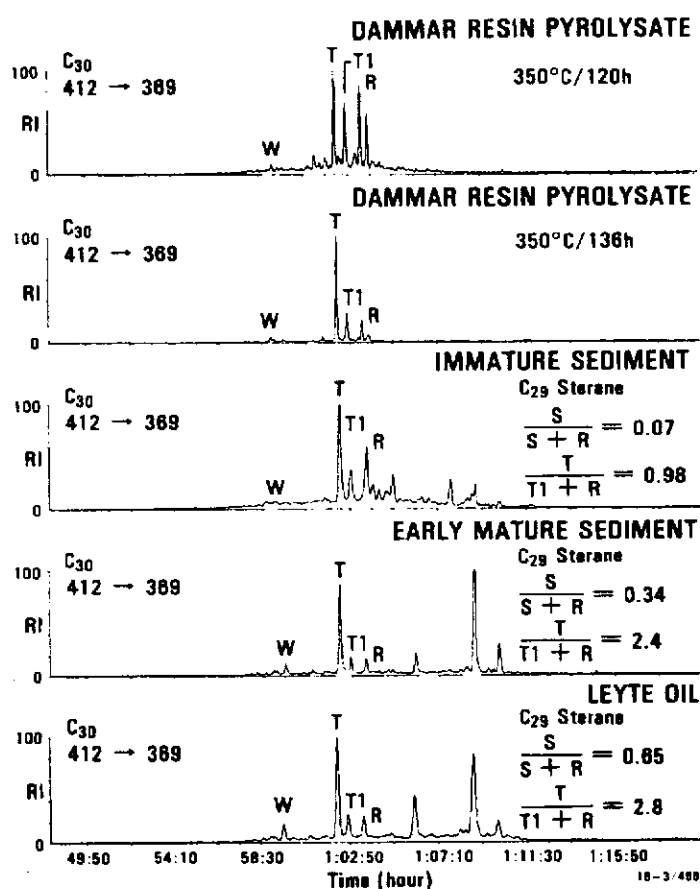
Figure 5.1 Partial MRM-GCMS chromatograms showing the bicadinane isomeric distribution in dammar resin pyrolysates, sediments and oils. C_{29} Sterane (S/S+R) and bicadinane isomer ratios (BMI 1 - see text) are also shown. RI = relative intensity.

BMI 1 appears to reach a maximum value when the sterane ratio is near 0.4, which equates to the onset of oil generation by conventional interpretation (Peters and Moldowan, 1993). BMI 2 and 3 also appear to maximise before

the sterane maturity parameter but it is difficult to say where this occurs because of the greater noise in the data.
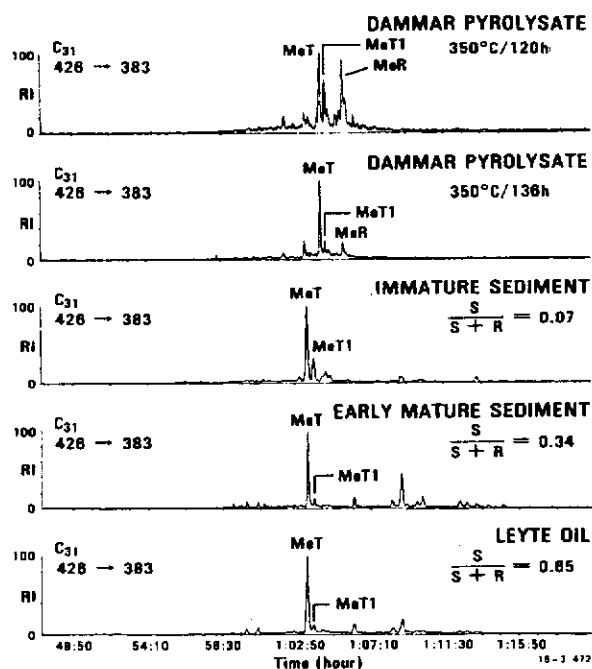
Figure 5.2 Partial MRM-GCMS chromatograms showing the methyl bicadinane isomeric distribution in resin pyrolysates, sediments and oils. RI = relative intensity.

If the bicadinane maturity indicators truly maximised before the sterane epimer ratio this would limit their use as maturity indicators for oils. However, evaluation of the indicators by reference to the sterane epimer ratio of these outcrop samples is unsatisfactory for several reasons: Firstly, as mentioned in the introduction, Tertiary-age oils (and by implication, sediment bitumens) have lower and more variable sterane maturities than those from older source rocks (Grantham, 1986). Secondly, there is no independent control on the kerogen maturity of the samples since the maximum paleotemperature is not known and a vitrinite reflectance measurement is available for only one sample (Table 5.1). Finally, many seep oils from the Visayan Basin are biodegraded and it is possible that biodegradation has increased the sterane epimer ratio for the more mature sediments as well. For these reasons, a more comprehensive study was carried out using downhole sediments from the South Sumatra Basin.
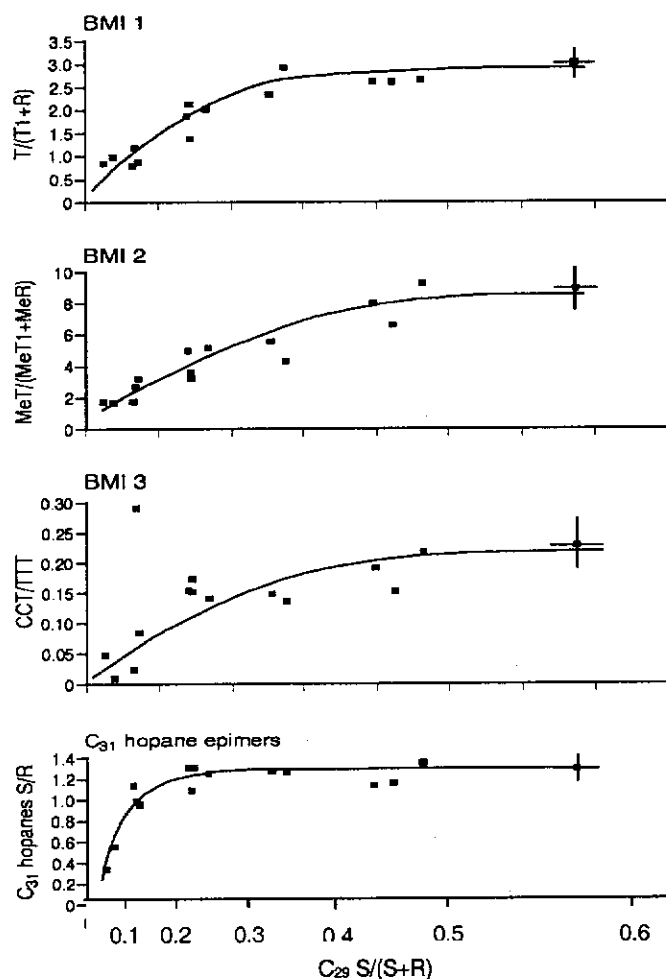
Figure 5.3   Variation in bicadinane against sterane based maturity indicators for Visayan Basin sediments. The C_{31} Hopane 22S/22R epimer ratio is included for comparison. Horizontal and vertical bars on the last point in each plot show the standard deviation for triplicate measurements. For definition of the maturity parameters see the text and Table 5.4.

5.4.2 Kerogen maturity and source character of the South Sumatra Basin sediments (GK well)

Profiles of present day temperature, TOC, vitrinite reflectance and Rock Eval T_{max} in the GK well are shown in Fig. 5.4. The estimated depth to onset of significant oil generation in the South Sumatra Basin (ca. 2100 m) is also marked on these and subsequent plots. This depth is only an estimate because no significant oil generation occurs in the GK well and Rock Eval production indices for cuttings do not exceed 0.1 even for the deepest coals (Table 2.2). The depth was derived by applying the burial and heat-flow history used previously for the South Sumatra Basin (Sosrowidjojo et al.

1994) to kerogen kinetics reported for Talang Akar Fm. coals (Noble et al. , 1991). There is a large uncertainty in the depth to onset of oil generation calculated in this way because, as Tegelaar and Noble (1993) have shown, kerogen kinetic properties vary widely, even within the classical Type I, II and III groups defined by hydrogen index. Furthermore, where the nature of the organic matter changes down-section (as it does in the GK well), there may be two or more overlapping "oil windows" corresponding to kerogens of differing thermal lability. Nevertheless, the coals of the Talang Akar Fm. are the main source of oil in the South Sumatra Basin and are representative of fluvio-deltaic source rocks across most of Southeast Asia. Gas chromatograms (Fig. 5.5) confirm that these coals first produce "oil-like" bitumens between 2000 and 2300 m.
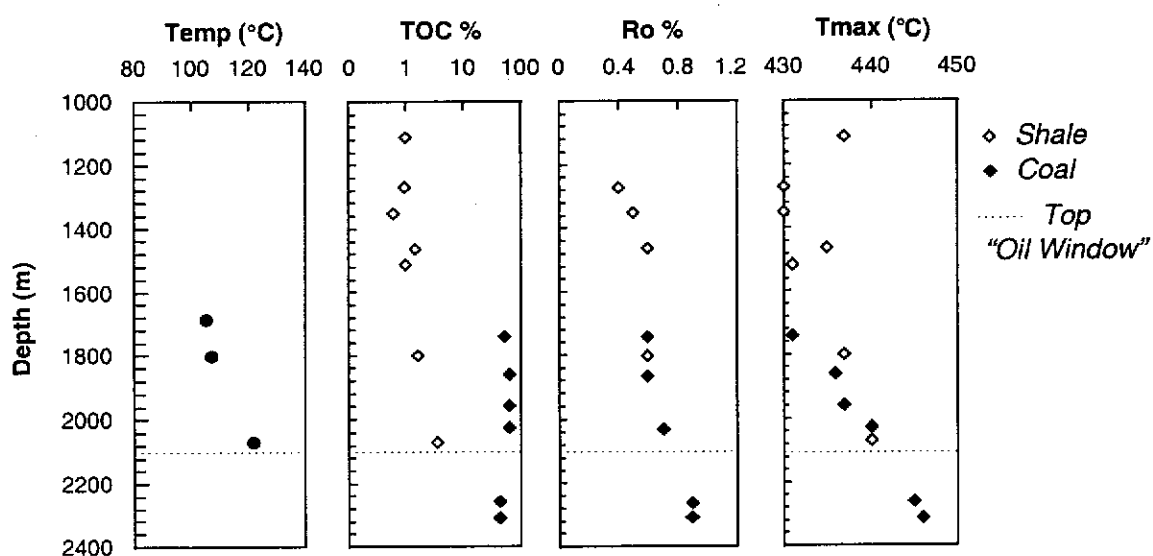
Figure 5.4   Variation of present day downhole temperature, total organic carbon, vitrinite reflectance and Rock Eval T$_{max}$ with depth in the GK well. The dotted line shows the modelled depth to onset of oil generation (see text). Downhole temperatures were measured in sandstones.

5.4.3 Source character of the GK sediments

Source matter type, depositional environment and/or source rock lithology affect all biomarker maturity indices to some extent (Dahl et al., 1993; Moldowan et al., 1986; Peters et al., 1990; Peters and Moldowan, 1993; ten

Haven et al., 1986; Strachan et al., 1989). Hence, it is necessary to consider how source character varies through the GK well section. Values for several biomarker indicators of source type are presented in Table 5.3. The variation of these indicators with depth is shown in Fig. 5.6. The marine shales of the Gumai and transitional Talang Akar Formations have relatively low pristane/phytane ratios (for this maturity) and a high proportion of C_{27} steranes due to a contribution from marine algae. 24-n-Propylcholestanes are also present in samples with the highest C_{27}/C_{29} sterane ratios, thus confirming the marine component (Moldowan et al., 1990; Peters and Moldowan, 1993). The apparent absence of these compounds in other samples does not exclude the possibility of a marine influence however, since a marine:terrestrial source contribution of less than about 20:80 might not yield detectable 24-n-propylcholestanes (as discussed in chapter three).

The trisnorneohopane ratio/trisnorhopane ratio (T_s/T_m) is known to respond to both source and maturity and some discussions of the source influence suggest that this is due to the catalytic effect of clay surfaces. In the GK well, T_s/T_m is more strongly correlated with the C_{27}/C_{29} sterane ratio ($r^2 = 0.75$) than with either depth or lithology per se (Fig. 5.6). In a study of Toarcian shales, Moldowan et al. (1986) found that T_s/T_m values were lower for organic matter deposited under more oxic/acid conditions and showed that conditions during early diagenesis were important in determining the starting point for many thermally-sensitive biomarker ratios. The C_{27}/C_{29} sterane ratio is only an indirect indicator of Eh/pH conditions during early diagenesis because a) deposition of terrigenous organic matter may occur under either terrestrial or marine conditions in a delta; and, b) Eh can be low or high in either setting. In general terms, however, a higher proportion of C_{27} steranes should correspond to more marine and therefore less acid conditions during early diagenesis and hence a reduced tendency toward acid-catalysed diagenetic reactions.

All of the GK samples contain oleananes, oleanoid triterpanes and bicadinanes derived from the angiosperm trees which dominated tropical lowlands during the Tertiary (see chapter six for details).
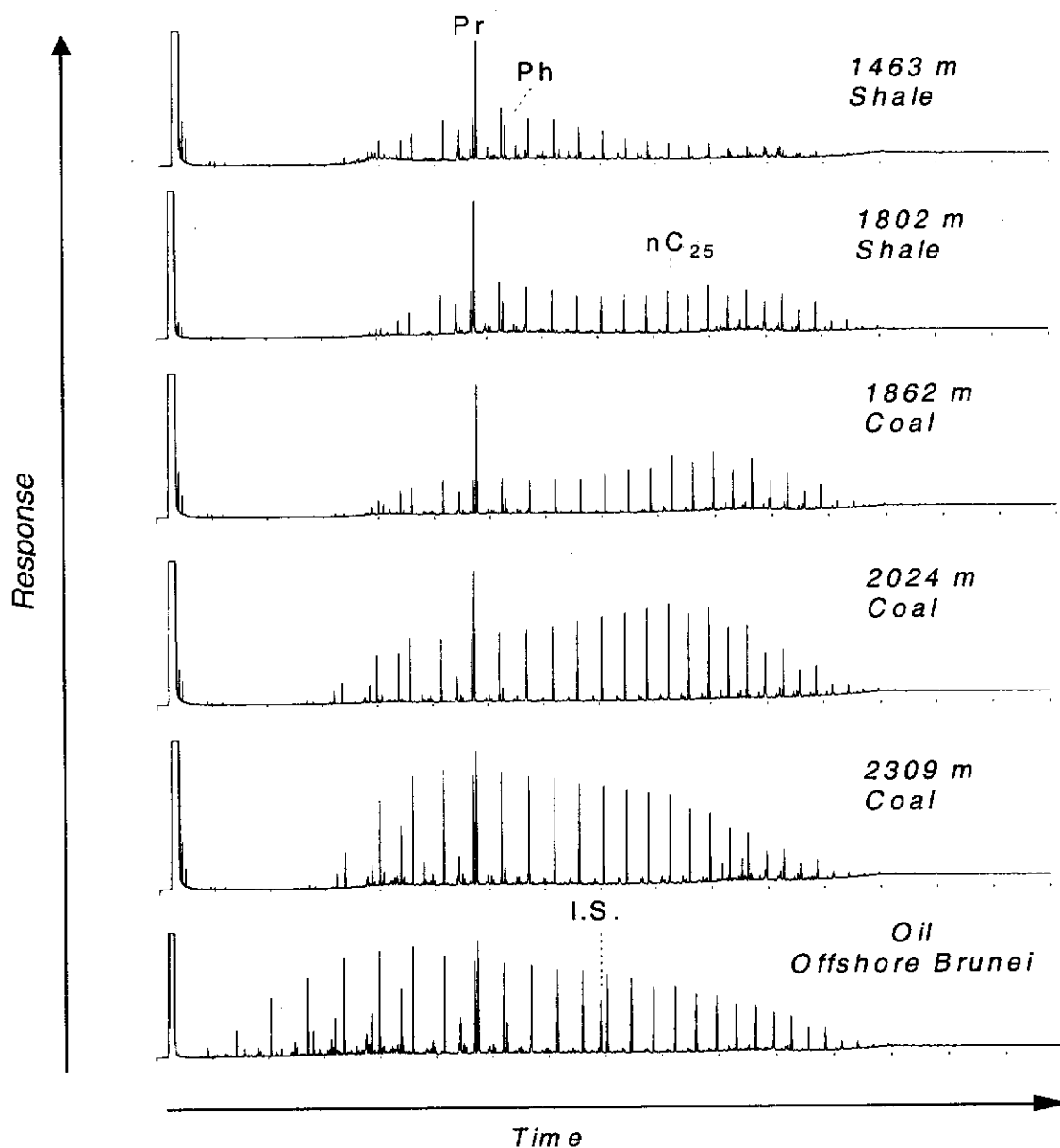
Figure 5.5   Gas chromatograms for the saturate fractions of sediments at various depths in the GK well and for a typical deltaic oil (from offshore Brunei; FD B2). I.S. = internal standard (3-methylheneicosane), Pr = pristane, Ph = phytane.

Table 5.3   Source and maturity indicators for sediments from the GK well, South Sumatra Basin (nd = not determined). See Fig. 5.7 and Table 5.4 for definitions.

Depth (m)	Source						Conventional Maturity			New Maturity				
	Pr/Ph	C_{27}/C_{29} Sts	%C_{30} Sts	Ts/Tm	C_{29} S/(S+R)	C_{31}H S/(S+R)	TA/(TA+MA)	TNR-1	MPI-1	BMI-1	DSR	DTR-1	DTR-2	I/(I+C)
1112	5.0	0.44	1.2	0.10	0.17	0.34	0.63	1.07	0.83	2.14	0.44	0.01	0.02	0.06
1268	4.2	1.07	3.2	0.49	0.08	0.41	0.70	1.01	0.72	1.34	0.38	nd	nd	0.05
1350	4.4	1.00	2.9	0.48	0.12	0.46	0.73	0.89	0.83	1.50	nd	0.01	0.09	0.07
1462	3.5	1.21	2.1	0.39	0.17	0.50	0.77	0.85	0.79	1.94	0.63	nd	nd	0.10
1512	6.0	0.46	1.8	0.24	0.36	0.59	0.84	0.89	0.78	2.98	0.55	0.14	0.20	0.08
1740	14.3	0.16	<1	0.03	0.48	0.60	0.97	0.75	0.66	2.85	0.72	0.29	0.24	0.10
1800	6.4	0.60	2.1	0.18	0.28	0.58	0.99	0.78	0.71	2.80	0.86	0.69	0.35	0.15
1860	15.0	0.03	<1	0.03	0.47	0.58	0.98	0.86	0.64	2.40	0.87	0.37	0.26	0.11
1958	12.6	0.06	<1	0.05	0.51	0.59	1.00	0.65	0.66	3.16	0.84	0.40	0.34	0.11
2024	11.4	0.10	<1	0.06	0.56	0.58	1.00	0.75	0.72	3.09	0.94	0.55	0.35	0.18
2068	8.8	0.32	<1	0.18	0.39	0.58	1.00	0.92	0.58	2.79	0.91	0.53	0.38	0.18
2258	11.3	0.15	<1	0.22	0.53	0.60	nd	0.90	0.69	3.91	1.00	0.81	0.42	0.25
2310	8.2	0.12	<1	0.24	0.55	0.59	nd	0.68	0.71	3.99	0.91	0.71	0.39	0.18
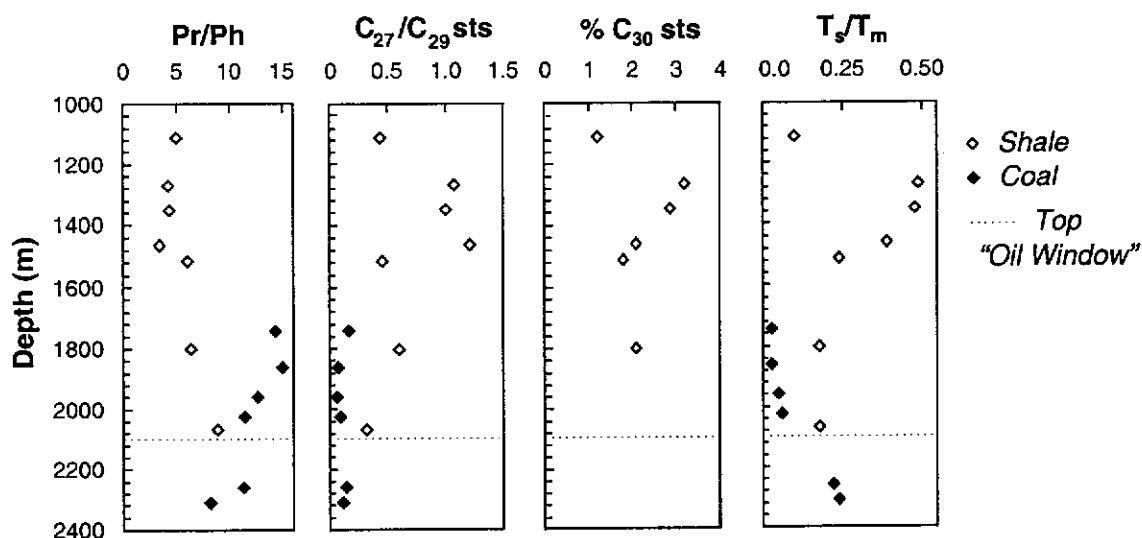
Figure 5.6   Changes in source-related characteristics with depth in the GK well. Pr/Ph = pristane/phytane, C_{27}/C_{29} sts = C_{27}/C_{29} total desmethyl steranes, %C_{30}sts = % 24-n-propyl cholestanes of the total C_{27} - C_{30} desmethyl steranes and T_s/T_m = Trisnorneohopane/Trisnorhopane.

5.4.4 Origin and definition of maturity indices

Partial GCMS chromatograms depicting maturity sensitive isomer
distributions of bicadinanes, diaromatic secobicadinanes, diaromatic
tricadinanes and cadalenes are shown in Fig. 5.7. Annotations to the
chromatograms show how each maturity index is defined and these are
summarised in Table 5.4. All the indices are empirical in the sense that the
reactions underlying them are not fully understood nor is it yet known
whether genuine conversions or differential rates of generation/destruction
are responsible for the changes observed.

The bicadinane maturity index (BMI-1) is the ratio of the peak area for
compound T to the sum of peak areas for compounds T1 and R. Compound
T has been identified as *trans-trans-trans* bicadinane (Cox et al., 1986) but
the structures of compounds T1 and R are not known. However, since their
mass spectra differ only slightly from that of compound T (Murray et al.,
1994a), they are presumed to have the *trans-trans-trans* ring configuration
and to differ from compound T in the ring position or axial/equatorial location
of the substituent groups. Other bicadinane maturity indices (BMI-2 and 3)
were not calculated for the South Sumatra Basin sediments because
interfering peaks prevented accurate measurement of the small W and MeT
peaks in the MRM-GCMS mass chromatograms. Compound W gives a more
prominent peak, relative to compound T, in SIM-GCMS m/z 191 mass
chromatograms.

van Aarssen et al. (1992a) tentatively identified and provided mass spectral
information for several C_{27} diaromatic secobicadinanes and C_{42} diaromatic
tricadinanes in some Southeast Asian oils. They also proposed a catagenetic
pathway whereby these compounds could form from polycadinene, with the
loss of an isopropyl group from the molecule, giving rise to the C_{27} and C_{42}
molecules.

Table 5.4   Definitions of maturity indicators and abbreviations used.

Indicator	Abbreviation	Definition
Sterane epimer ratio	C_{29} S/(S+R)	C_{29} $\alpha\alpha\alpha$ 20S/(20S+20R) 24-ethylcholestane
Homohopane epimer ratio	C_{31}H S/(S+R)	C_{31} 22S/(22S+22R) 17α,21β-homohopane
Tri- to monoaromatic steroid ratio	TA/(MA+TA) ◢	C_{28}TA/(C_{29}MA+C_{28}TA). See Peters and Moldowan (1993).
Trimethylnaphthalene ratio	TNR-1	2,3,6-TMN/(1,4,6-TMN+1,3,5-TMN)
Methyl Phenanthrene Index	MPI-1	1.5 x (2-MP+3-MP)/(P+1-MP+9-MP)
Bicadinane Maturity Indicator	BMI-1	T/(T1+R). See Fig. 5.7A
Diaromatic Secobicadinane Ratio	DSR	D2/(D2+D6). See Fig. 5.7B and Sosrowidjojo et al. (1993).
Diaromatic Tricadinane Ratio - 1	DTR-1	DT1/(DT1+DT2). See text and Fig. 5.7C
Diaromatic Tricadinane Ratio-2	DTR-2	DT3/(DT1+DT3). See text and Fig. 5.7C
Isocadalene Ratio	I/(I+C)	Isocadalene/(Isocadalene+Cadalene). See Fig. 5.7D and Alexander et al., (1994).

Subsequently, Sosrowidjojo et al. (1993) identified the corresponding intact C_{30} and C_{45} molecules in some Indonesian crude oils and suggested that the abundance of these compounds relative to their des-isopropyl analogs was maturity dependent. The maturity indices DSR and DTR-1 (Fig. 5.7) record the relative proportion of des-isopropyl to intact diaromatic secobicadinanes and tricadinanes respectively. DTR-2 reflects changes in the internal ratio of two isomeric C_{42} diaromatic tricadinanes of unknown structure.

The isocadalene/cadalene ratio was proposed by Alexander et al. (1994) as an alternative to other aromatic maturity indices for post-Triassic sequences showing terrestrial influence. Cadalenes are widespread in sediments containing higher plant organic matter and, unlike the bicadinanes, probably have a more general source than polycadinene (Simoneit et al., 1986 and references therein). Nevertheless, they are commonly abundant in sediments

containing bicadinanes and related compounds and such sediments also contain high concentrations of the des-isopropyl analog of cadalene, 1,6-dimethylnaphthalene (Alexander et al., 1994; Noble et al., 1991; Radke et al., 1994). The latter observation, together with the results of laboratory heating experiments, led Alexander et al. (1994) to conclude that a direct product-precursor relationship exists between cadalene and isocadalene.

Figure 5.7A

B

C_{30}

C_{27}

Diaromatic Secobicadinanes

$$DSR = \frac{D2}{D2 + D6}$$

$m/z = 362 \rightarrow 156$
80%

1270 m

D2

D3

D4

D1

$m/z = 404 \rightarrow 198$
100%

D6

D7

D8

D5

Response

100

50

0

100

50

0

58   60   62   64   66   68

Retention Time (min)

Figure 5.7B

C

Diaromatic Tricadinanes

C_{45}

C_{42}

$$DTR\,1 = \frac{DT1}{DT1 + DT2}$$

$$DTR\,2 = \frac{DT3}{DT1 + DT3}$$

$m/z = 156$
100%

DT1

DT3

2310 m

$m/z = 198$
41%

DT2

Response

100

50

0

100

50

0

72   76   80   84   88   92

Retention Time (min)
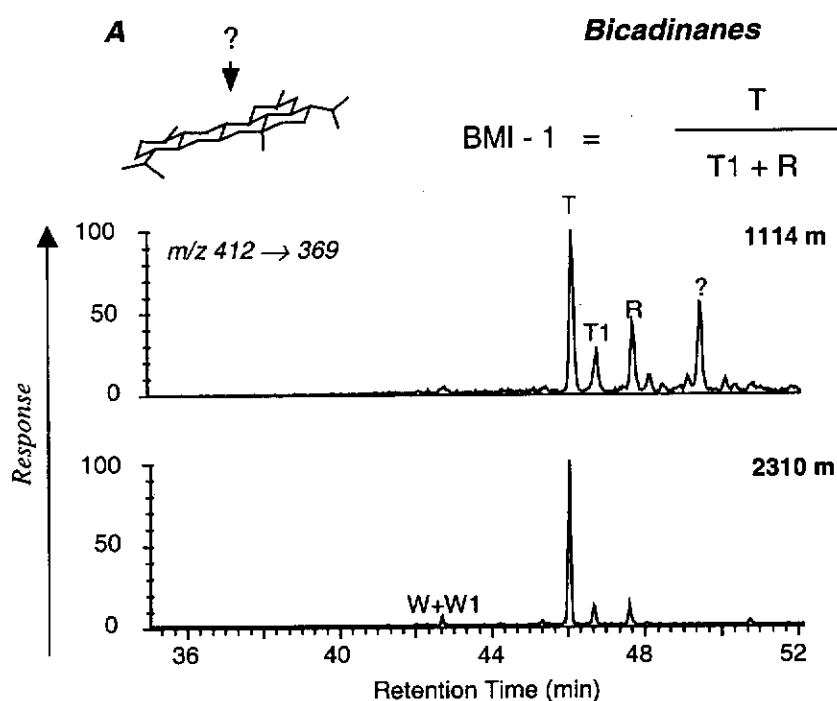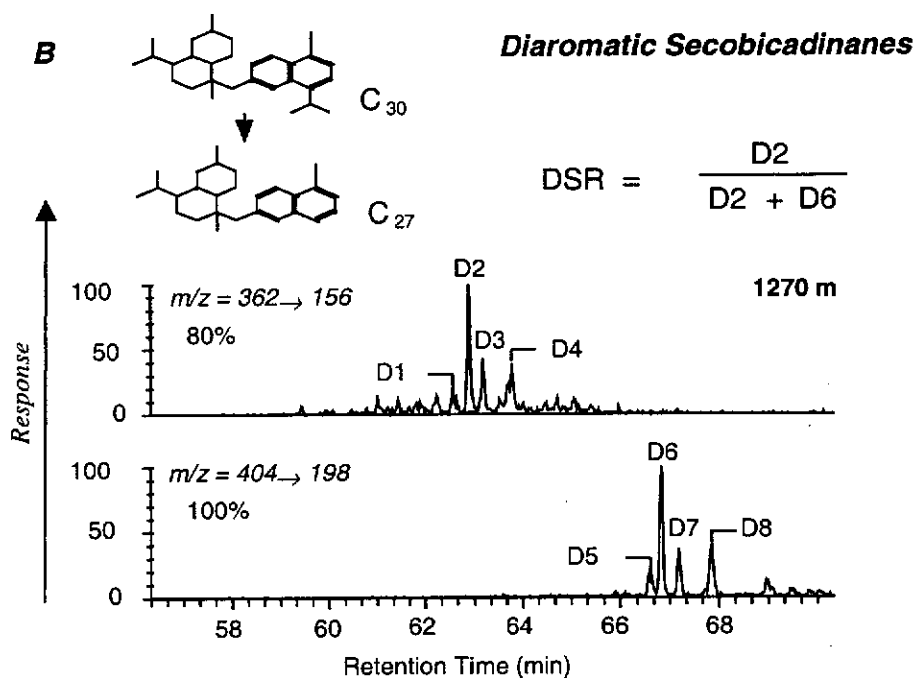
Figure 5.7C
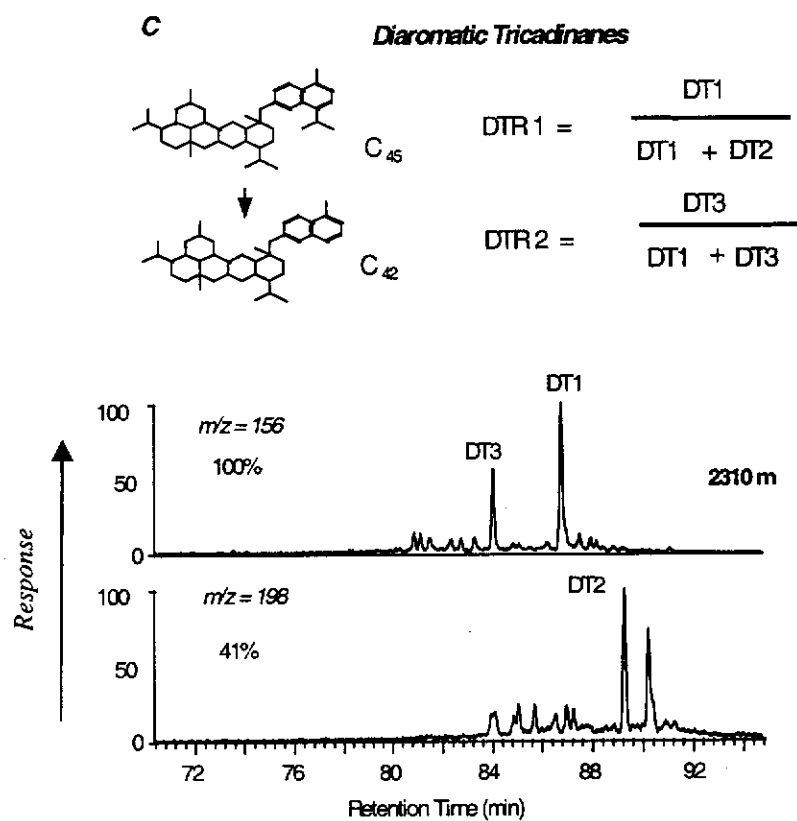
$$\text{Isocadalene ratio} = \frac{I}{I + C}$$
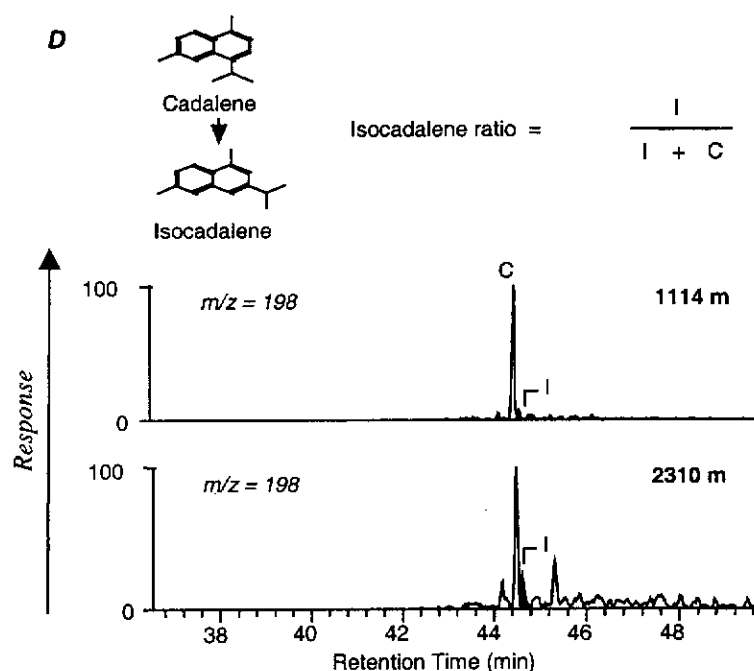
Figure 5.7D

Figure 5.7A-D   Partial GCMSMS and SIM-GCMS chromatograms showing derivation of polycadinene-related maturity indicators.

5.4.5 Variation in maturity indices with depth and relation to the "oil window"

Values for five conventional and five polycadinene-related maturity indices for the GK sediments are given in Table 5.3, while the progress of the five conventional biomarker maturity indices with depth is shown in Fig. 5.8. The hopane and aromatic steroid indices reach maximum values above 1500 m and before the predicted onset of oil generation for the coals. The trimethylnaphthalene ratio (TNR-1) and methyl phenanthrene index (MPI-1) fail to show an increase with depth, which is a consequence of the strong source and diagenetic control on aromatic isomer distributions in terrigenous sequences, especially at low to moderate maturity (Strachan et al., 1988). The failure of these indices emphasises the need for alternatives.
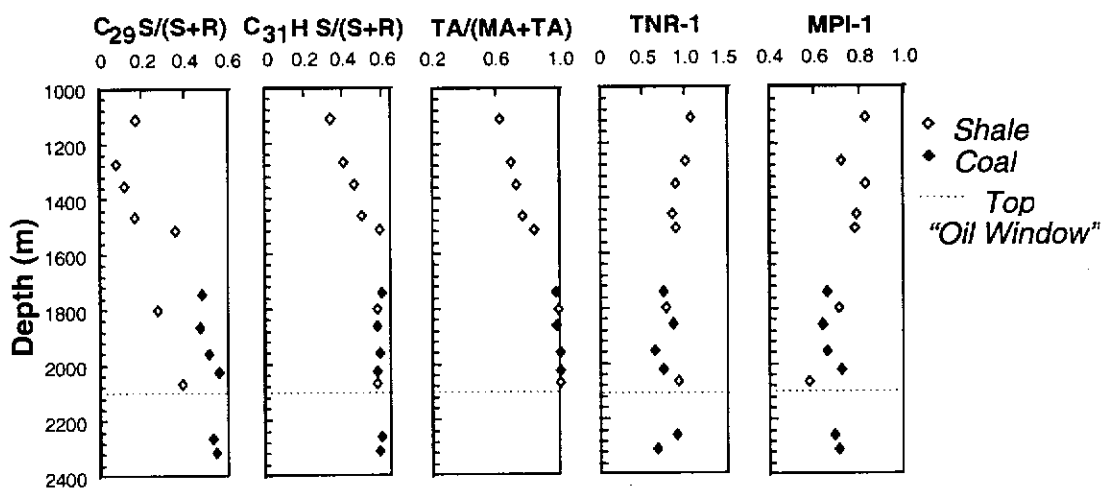
Figure 5.8 Variation with depth of five conventional maturity indices in the GK well: C_{29} $\alpha\alpha\alpha$ 20S/(20S+20R) steranes, C_{31} 22S/(22S+22R) homohopanes, tri- to monoaromatic steroid ratio, trimethylnaphthalene ratio (TNR-1) and methyl phenanthrene index (MPI-1). See Table 5.4 for definitions. The dotted line shows the modelled depth to onset of oil generation.

Although the C_{29} sterane epimer ratio shows the expected increase with depth (Fig. 5.8), it also clearly responds to the degree of terrestrial/marine influence on the source (as shown by the C_{27}/C_{29} sterane ratio, Fig. 5.6). Indeed, the correlation with C_{27}/C_{29} steranes ($r^2 = -0.83$) is stronger than that with depth ($r^2 = 0.76$). Strachan et al. (1989) reported differences between the sterane maturities of coal-shale pairs and argued that either coals or shales could give higher values depending on the heating rate. However, at heating rates typical of the South Sumatra Basin, their results suggested that shales should give values higher than coals, whereas the converse situation occurs here. In contrast, Hoffmann et al. (1984) found no difference in the sterane epimer ratios of coal/shale pairs from the Mahakam Delta. Such contradictions probably arise from the difficulty in distinguishing between source rock lithology and the conditions under which diagenesis of the organic matter took place. The land plant matter present in deltaic marine shales may represent primary deposition via fluvial transport or it may be material redeposited following erosion from coastal peat swamps. In the former case, early diagenesis will have taken place under alkaline conditions while in the latter, acid conditions will have been prevalent, at least in the

aqueous phase. Moldowan et al. (1986) noted higher values for the sterane maturity index in Toarcian shales deposited under more oxic and more acid conditions and suggested that this could be due to acid-catalysed, diagenetic epimerisation of steroids having a side-chain double bond. The data in Fig. 5.8 are consistent with this explanation if it is assumed that samples containing more marine organic matter (i.e., higher C_{27}/C_{29} sterane ratio) contain proportionally less material which has experienced the acid conditions of a peat swamp. It should be mentioned that this argument rests on differences in bulk solution pH between marine and terrestrial environments whereas the acidity/alkalinity of particle surfaces may be more relevant to the reactions concerned.

The variation of the five polycadinene related maturity indices with depth in the GK well is shown in Fig. 5.9. The bicadinane maturity index (BMI-1) shows the expected increase with depth and, for the deeper samples at least, does not respond to variation in lithology or source character to the same extent as the sterane epimer ratio. The top of the oil window corresponds to a BMI-1 value of about 3 and the value continues to increase with increasing depth. Data obtained recently for another well in the South Sumatra Basin (details in Sosrowidjojo et al., 1994), show an average BMI-1 value of 3.7 for sediments which are at or near peak oil generation. Recent work by Stout (1995) on sediments from the Mahakham Delta suggests that BMI-1 = 2.8 - 3.0 corresponds to R_o = 0.5 - 0.6 and hence to the onset of significant oil generation.

The aromatic secobicadinane, aromatic tricadinane and isocadalene indices (DSR, DTR-1, DTR-2 and (I/(I+C)) all increase with increasing depth. However, for DTR-1 and DTR-2 and the isocadalene index, the shale at 1802 m gave values markedly higher than the coals at similar depth.
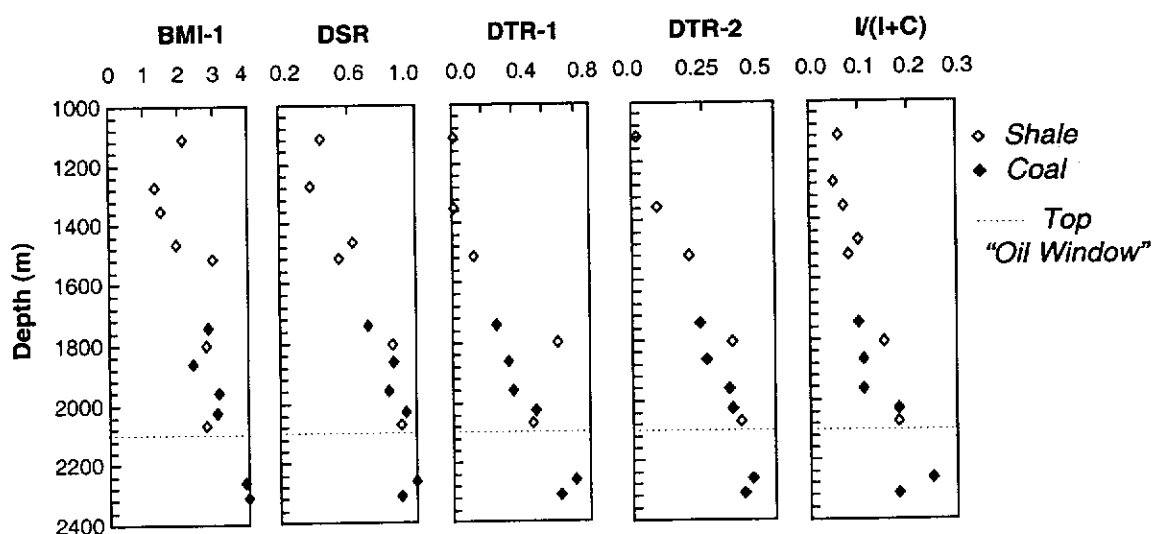
Figure 5.9 Variation with depth of five polycadinene related maturity indicators in the GK well: bicadinanes (BMI-1), diaromatic secobicadinanes (DSR), diaromatic tricadinanes (DTR-1 and -2) and isocadalene index (I/I+C). See the text, Table 5.4 and Fig. 5.7 for definitions. The dotted line shows the modelled depth to onset of oil generation.

Although little emphasis can be placed on deviation of a single point, this may be evidence of a source or lithology effect on the loss or rearrangement of the isopropyl group. There are two indirect pieces of evidence to support this view. First, Alexander et al., (1994) demonstrated that acid-clays promote the loss and transfer of the isopropyl group from cadalene *in-vitro* and presented evidence that these reactions occur under natural conditions. Second, a homologous series of alkyl and des-alkyl bicadinanes has been observed in oils, resin pyrolysates and sediments (Murray et al., 1994a; Australian Geological Survey Organisation, unpublished) and preliminary observations suggest that their abundance is highest in shales. The factors which promote the removal or transfer of the isopropyl group do not appear to be the same as those associated with the formation of neohopanes, as no correlation between T_s/T_m and the abundance of des-isopropyl bicadinanes in oils is observed. Given that the facies effects on T_s/T_m (and on sterane epimeric ratios) probably operate during *diagenesis* (Moldowan et al., 1986) and those on the bicadinanes during *catagenesis*, this lack of correlation is understandable.

If a shale lithology encourages loss or rearrangement of the isopropyl group DSR should deviate at 1802 m as well, since this index also records the loss of an isopropyl group. However, the data in Fig 5.9 suggests that DSR is already near its maximum value at this depth, perhaps leaving little scope for a facies related enhancement.

5.4.6 Polycadinene-related maturity indices for oils and comparison of maturity parameters for oils and sediments

Values for the sterane epimer ratio and for polycadinane-related maturity indices for 17 oils are given in Table 5.4. It was not possible to obtain aromatic bicadinane and isocadalene/cadalene maturity indices for all of the oils because many did not give large enough or well enough resolved peaks in mass chromatograms of the aromatic fractions. This was especially so for the aromatic tricadinanes where the intact C_{45} isomers, although abundant in the sediments, were mostly not detected in the oils. Likewise, the least abundant of the two C_{42} aromatic tricadinanes (DT3) could not be reliably detected in any of the oil samples and so no values are available for DTR-2 in oils. A different problem arose for isocadalene and cadalene which, although commonly abundant in the oils, were poorly resolved from each other and from other alkyl naphthalenes. These problems are partly operational in nature as the GCMSMS and GCMS methods are not as selective for the aromatic compounds as they are for the saturated bicadinanes.

Crossplots of one maturity indicator against another are useful in detecting anomalies, whether they be related to the indicator themselves or to some peculiarity of the sample. Crossplots of the five polycadinene-related maturity indices against the sterane index for the South Sumatra Basin sediments and the oil set are shown in Fig. 5.10.

Table 5.4   Sterane epimer ratio and polycadinene-related maturity indices for oils. Refer to Fig. 5.7 for abbreviations.

Number	Sterane C_{29} S/(S+R)	BMI-1	DSR	DTR-1	I/(I+C)
FD 1	0.53	4.3	-	-	-
FD 2	0.26	2.9	0.57	0.70	0.18
FD 3	0.52	3.5	0.99	-	0.67
FD 4	0.48	2.8	-	-	0.48
FD 6	0.52	2.8	0.83	0.85	0.11
FD 9	0.51	3.4	0.94	0.90	0.16
FD 10	0.37	3.3	0.79	-	0.04
FD 11	0.53	2.9	-	-	0.25
FD 12	0.54	3.7	0.99	0.95	0.49
FD 13	0.51	2.9	0.92	-	0.34
Conf.	0.29	3.0	0.54	-	0.09
Conf.	0.27	2.8	0.99	-	0.36
Conf.	0.43	2.7	0.85	-	0.28
FD B1	0.41	3.9	-	-	0.15
FD B2	0.23	4.1	-	-	0.11
FD P	0.44	3.1	-	-	-
MC 4	0.52	3.3	-	-	-

The plot for BMI-1 (Fig. 5.10) shows a reasonably smooth curve for the sediment samples and the BMI values for oils mostly fall within in the region judged to be the "oil window" for Talang Akar coals. However, there is some indication that BMI-1 continues to increase beyond the point where the sterane epimer ratio has reached its *pseudo*-equilibrium value of 0.55. This contrasts with the data for the Visayan Basin sediments where BMI-1 appeared to maximise before the sterane index. However, the Visayan Basin sediments are outcrop samples and it is possible that the sterane index has been affected by biodegradation for some samples. If this is so, the true range of maturities may be narrower than that suggested by the sterane epimer ratios. Data published by Stout (1995) also indicates that BMI-1 continues to increase into the oil window.

The diaromatic secobicadinane and isocadalene indices show poor correlation with the sterane index for both sediments and oils. This is probably because the catagenetic facies effects on the aromatic bicadinanes and cadalenes operate in the opposite sense to the diagenetic effects on the steranes.
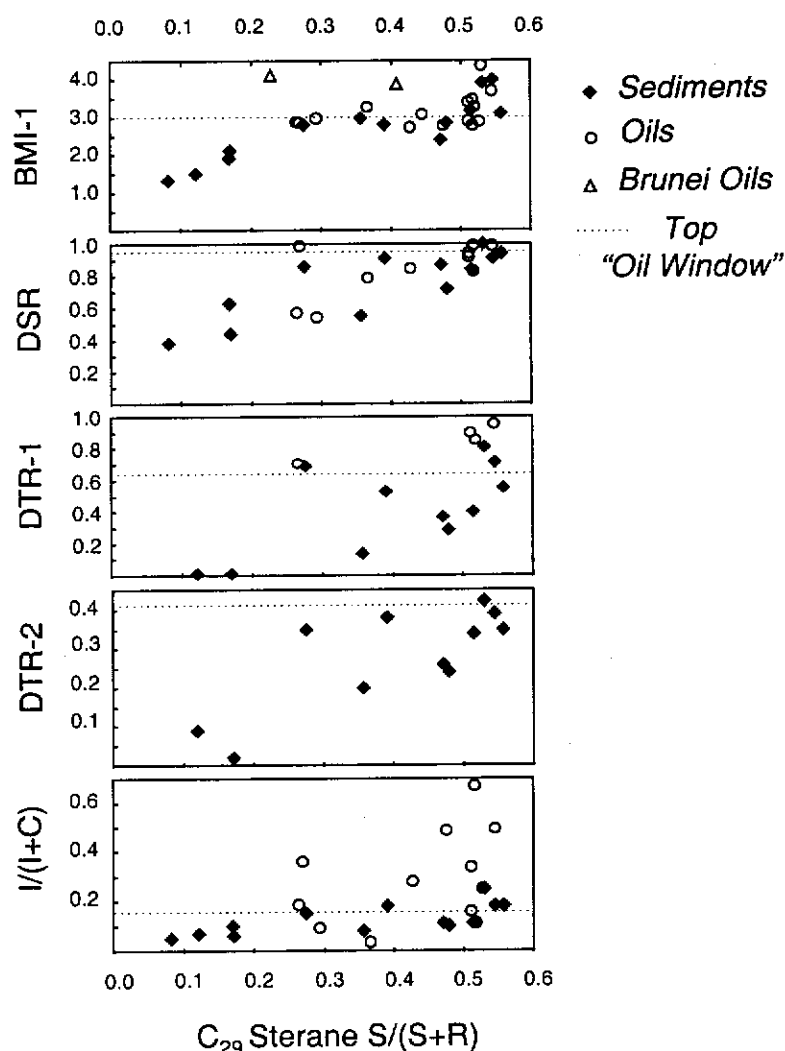
Figure 5.10 Crossplots of polycadinene-related maturity indicators against the sterane maturity index for sediments of the GK well and for oils from various locations. The dotted lines show the approximate threshold values for oil generation determined from the depth *vs.* maturity plots in the GK well.

Hence, the crossplots tend to emphasise the facies dependence of the aromatic indicators and obscure the maturity related response. The poor correlation between the sterane and aromatic indices could also be due to the oils having picked up immature terrigenous material during migration but, if this were the case, one would expect BMI-1 to correlate poorly with the sterane index as well.

Two of the oils shown in the plot for BMI-1 are from offshore Brunei and were included by Grantham (1986) in his study of the biomarker maturity of

Tertiary oils. These two oils (open triangles, Fig. 5.10) plot away from the trend in that they have normal bicadinane maturities and yet low to very low sterane maturities. There is little doubt that the bicadinane maturity indicator is the more valid measure of the bulk hydrocarbon maturity of these oils since the n-alkane distribution of the oil with the lowest sterane maturity (gas chromatogram shown in Fig. 5.5) suggests moderate to high maturity generation. Also, notwithstanding the limitations of aromatic maturity indicators discussed earlier, the values of MPI-1 and TNR-1 for this oil (0.96 and 0.92 respectively) both indicate generation within the normal oil window.

The explanation for the low sterane epimer ratio of the two Brunei oils cannot be the general one offered by Grantham (1986) for the low sterane maturity of Tertiary oils, i.e. that high heating rates caused sterane equilibration before the main phase of oil generation. This is so because, although the two oils have very different epimer ratios, they come from the same basin, and their source rocks should thus have experienced broadly similar heating rates. Also, first-order kinetic models of sterane pseudo-epimerisation (Marzi et al., 1990) with respect to those for kerogen transformation (Tegelaar and Noble, 1993) do not support a significant dependence on heating rate for the sterane maturity of oils. This is illustrated in Fig. 5.11 using the sterane kinetics invoked by Grantham (i.e., those of Mackenzie and Mackenzie, 1983) as well as parameters more recently determined by Marzi et al. (1990). The heating-rate effect on sterane epimerisation for oils (as opposed to sediments), depends only on the relatively small difference between the time-temperature function for sterane pseudo-epimerisation and that for catagenesis of typical kerogens. Thus, an unrealistically high heating rate (near 20 °C Ma^{-1}) must be postulated to obtain the sterane epimer ratio observed for one of the Brunei oils, even using the more time-dependent kinetics of Mackenzie and Mackenzie. There is no indication that such rapid heating occurred in the offshore Brunei Basin (Ellenor, 1984).
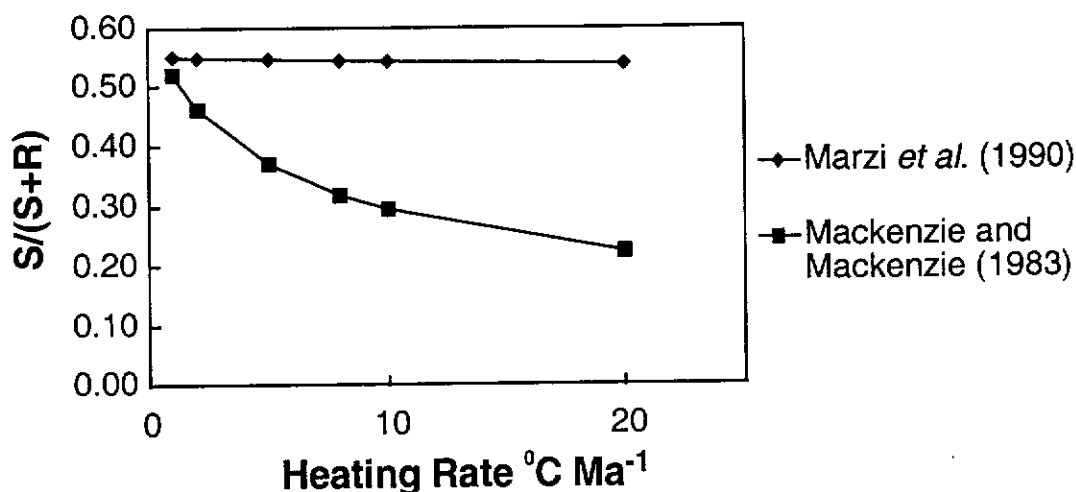
Figure 5.11   Variation in the calculated C_{29} sterane $\alpha\alpha\alpha$ 20S/(20S+20R) epimer ratio at the onset of oil generation (10 % kerogen transformation) as a function of geological heating rate. The plot is based on the kinetic parameters for sterane *pseudo*-epimerisation published by Mackenzie and Mackenzie (1983) (squares) and Marzi et al., (1990)(diamonds). For purposes of standardisation, the kerogen kinetic parameters used are those of the Kimmeridge Shale reported by Tegelaar and Noble (1993) but substitution of other kerogens does not significantly affect the depicted relationship.

Apart from diagenetic influences, which were discussed earlier, there are several alternative explanations for the low sterane maturity of the Brunei oils and for Tertiary oils generally. These include contamination with less mature organic matter during migration or in the reservoir and biodegradation of an early phase oil followed by overprinting. Grantham (1986) argued that such phenomena could not provide a general explanation for the low sterane maturity of Tertiary oils since oils from older source rocks should be affected with equal frequency. However, almost all of the Tertiary-age oils included in his study were of deltaic origin and more than half originated either from Brunei or from adjacent basins in North Borneo. Thus, the data set did not provide the means to distinguish between source rock *age* and *depositional setting* as the causative factor in low biomarker maturity. Most well-documented examples of contamination of oil with low maturity organic matter, either during migration or in the reservoir, refer to deltaic petroleum systems (e.g., Hoffmann et al., 1984; Morelos-Garcia et al., 1993; Philp et al., 1982). It therefore seems likely that the low sterane isomerisation

reported for many Tertiary-age deltaic oils is at least partly due to entrainment of low maturity organic matter in the reservoir or during migration.

5.4.7 Resistance of bicadinanes to biodegradation

Partial MRM-GCMS chromatograms for two seep oils from the Philippines are shown in Fig. 5.12. Both oils are derived from the same source (TR type) but one has been biodegraded to an extent described as "very heavy" (level 8 of Peters and Moldowan, 1993). At this level of biodegradation the C_{30} hopane has been almost completely removed, causing relative enrichment of the more resistant oleanane and gammacerane. The regular steranes have also been depleted and, as generally observed (Peters and Moldowan, 1993), the R epimer has been affected more than the S epimer, thereby invalidating any maturity information obtainable from their ratio. Furthermore, oil-source and oil-oil correlation is severely hampered by the distortion of the biomarker profile which has occurred. However, the bicadinane isomer distribution is unaffected and can be used to set limits on the maturity of the oil as well as to develop biodegradation resistant source correlation parameters (e.g., see Curiale et al. 1994).

5.5 Conclusions

This study has shown that several polycadinene-related indices increase with increasing thermal stress and continue to change into the oil window. This observation should help explorationists to reduce the range of possibilities for the location of the oil window and reveal instances of mixing, migration contamination, and low maturity generation. The bicadinane maturity index (BMI-1) should be useful in constraining the maturity of many Southeast Asian and some Australasian oils and has several advantages over the sterane maturity index for such samples: a) it continues to change into the oil window and beyond the point where the sterane index has maximised b) it is

less affected by diagenetic facies effects because the relevant compounds are mostly bound in a polymer during diagenesis c) it remains unaffected at levels of biodegradation sufficient to invalidate sterane and hopane based indices.
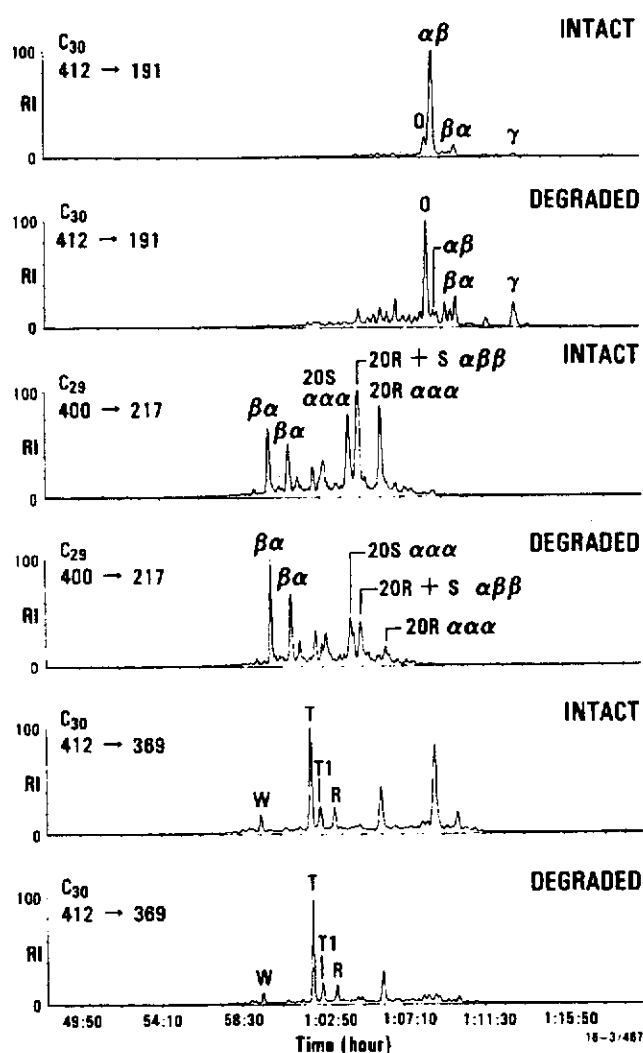
Figure 5.12 Partial MRM-GCMS chromatograms of C_{30} triterpanes, C_{29} steranes and bicadinanes in intact and very heavily biodegraded oils. See Table 3.2 for a key to peak annotations.

The main disadvantage of BMI-1 is its obvious restriction to samples containing bicadinanes. However, bicadinanes are present in virtually all the

Tertiary oils and sediments of Southeast Asia, many from Southern China and India as well as terrigenous facies of New Zealand and some parts of Australia (Summons et al., 1995). Another disadvantage of BMI-1 is our present lack of knowledge of the structure of the compounds used for the index. However, the availability of a well characterised and relatively simple precursor material (polycadinene) should allow the determination of these structures as well as facilitating study of the reaction kinetics. Hopefully this will result in kinetic parameters which are better constrained than those currently available for the sterane and hopane reactions.

Maturity indices based on aromatic polycadinene derivatives also have the advantages of continuing to change into the oil window and being relatively resistant to biodegradation (Alexander et al., 1994; Sosrowidjojo et al., 1994). However, due to facies effects operating during catagenesis, they are likely to be applicable only where source rock lithology is invariant or where its effects can be taken into account. Furthermore, the aromatic tricadinane indices for oils could not be consistently measured due to low concentrations of the key compounds and poor resolution from other aromatics. Application of more selective analytical methods might improve this situation.

The polycadinene related indicators provide a means of assessing catagenetic maturity without significant diagenetic interference. This should help to determine whether (as currently assumed) the sterane maturities of oils are significantly affected by the rate at which their source rocks have been heated and to identify instances of true low-maturity generation.

CHAPTER 6: OLEANANES IN OILS AND SEDIMENTS: EVIDENCE OF MARINE INFLUENCE DURING EARLY DIAGENESIS

6.1 Introduction

The oleananes (Fig. 6.1) are formed in sediments through diagenetic and catagenetic alteration of various 3β-functionalised angiosperm triterpenoids (Rullkötter et al., 1994 and references therein). Being diagnostic of both source rock age and a land plant contribution they are important molecular fossils in petroleum geochemistry (Moldowan et al., 1994; Peters and Moldowan, 1993). Nevertheless, several observations show that the abundance of oleananes in an oil or sediment is not simply controlled by the amount of land plant contribution to the organic matter. First, the oleanane/hopane ratio of unbiodegraded oils falls in a narrow range (0 - ~ 3) regardless of the extent of land plant contribution, as inferred from other biomarker and geological information. For example, the oleanane/hopane ratio of 271 Tertiary-age oils from the Far East varies between 0. 01 and 2.9 (C. Schiefelbein, Geomark Research Inc., personal communication). This contrasts with the behaviour of another group of angiosperm markers, the bicadinanes, whose abundance in such oils can vary over three orders of magnitude (chapter three, Fig. 3.4). Second, some oils from marine source rocks contain abundant oleananes, even though carbon isotopes show only a minor land-plant contribution (chapter three, Figs. 3.4 vs. 3.10). Finally, in fluvio-deltaic systems where the marine/terrestrial character of the source varies with distance from the paleo-shoreline, oleanane/hopane does not always correlate with other indicators of land-plant content (e.g. $\%C_{29}$ steranes) or inversely with indicators of marine influence such as $\%C_{30}$ or C_{28} desmethyl steranes (e.g., Beaufort-McKenzie Delta, McCaffrey et al., 1994; Niger Delta, S. Sundararaman pers. comm.) Using a combination of

measured and interpolated data, Udo and Ekweozor (1990) found a correlation between % vitrinite (a land-plant related maceral) and oleanane/hopane in sediments of the Niger Delta. However, their data show no significant correlation when only the measured values are included.

In support of the use of oleananes as age markers, Moldowan et al. (1994) demonstrated a relationship between oleanane/hopane, source rock age and fossil evidence for the rise of the angiosperms during the Cretaceous (chapter one, Fig. 1.7). These workers used only sediments from deep marine basins in their study, so as to avoid the effects of local variation in plant community and depositional environment. In contrast, Killops et al. (1994b, 1995) used the abundance of oleananes relative to diterpanes to infer source age within the mainly fluvio-deltaic Taranaki Basin (New Zealand).

A difficulty with the use of oleananes as age and source markers in terrestrial systems is that the main fate of the precursor oleanenes in coal swamps and lakes is not hydrogenation but partial or complete aromatisation (Fig. 6.1). Progressive aromatisation, beginning soon after deposition and probably microbially mediated (Lohmann, 1988), produces pentacyclic hydrocarbons with from one to five rings aromatised (Chaffee and Fookes, 1988; Chaffee and Johns, 1983; Rullkötter et al., 1994; Spyckerelle et al., 1977; Stout, 1992; ten Haven et al., 1992a). Skeletal alteration involving contraction, loss, opening or cleavage of the A and C rings may be chemically or photochemically initiated (Chaffee et al., 1984; Corbet et al., 1980; Ellis et al., 1996; Hazai et al., 1989; Smith et al., 1995; Spyckerelle et al., 1977; Trendel, 1985; Trendel et al., 1989). Such reactions produce seco-oleanoids as well as mono- and bicyclic compounds which can only be recognised as fragment pentacyclanes by their substitution pattern, e.g. 1,2,7-trimethylnaphthalene arising from the D/E ring of oleanoids (Strachan et al., 1988). Further aromatisation of the intact skeleton and of cleavage products occurs with increasing thermal stress during burial (Hayatsu et al., 1987; Strachan et al., 1988). Clearly, oleananes can only occur in a sediment or oil

to the extent that the precursor molecules escape these reactions. Hence, their abundance is likely to be highly sensitive to changes in Eh and pH during early diagenesis.
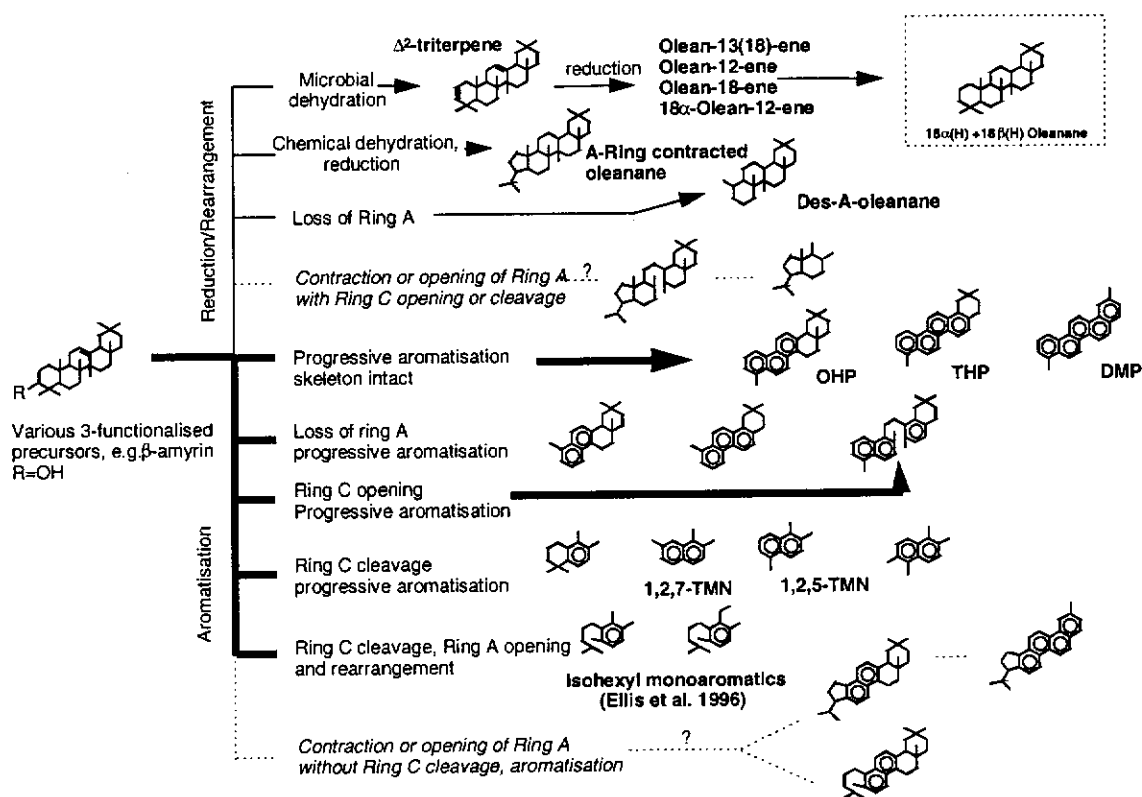
Figure 6.1 Summary of some processes leading to formation of saturated and aromatic oleanoids from 3-functionalised precursors. The diagram is illustrative rather than exhaustive and many more compounds have been identified - see references listed in the text, especially, ten Haven et al., (1992a,1992b), Stout (1992), Rullkötter et al., (1994) and references therein, Smith et al., (1995), and Ellis et al. (1996). Dotted lines lead to compounds which have not yet been identified but might result from combination of the known pathways. Thicker lines emphasise the dominance of aromatisation processes in non-marine sediments. OHP, THP, DMP = octahydro-, tetrahydro- and dimethylpicene.

In this chapter, evidence is presented that a marine influence during early diagenesis increases the abundance of oleananes in sediments and oils and reduces skeletal alteration and aromatisation. This influence may occur by marine overprinting of in-situ terrestrial organic matter or via redeposition of

peat organics in marine sediments. Only compounds with the oleanane skeleton are considered as these appear to be the most stable of the plant derived triterpenoids (Rullkötter et al., 1994). For example, it has recently been shown that lupenes can be converted to taraxastenes and oleanenes under acid conditions (Perkins et al., 1995).

6.2   Samples

The sediments used for this study are from the Buller Basin (New Zealand), Southeast Luzon Basin (Philippines) and South Sumatra Basin (Indonesia). Details of location, depth and age are given along with some basic geochemical data in Table 2.2. However, a summary relevant to the purposes of this chapter is given below:

The "Buller Coals" are composite core sections from Coal Research Limited (NZ) drillhole 1281/1494. They are of Eocene (Bortonian) age and further description can be found in Norgate (1995) and Newman (1991). The stratigraphy as observed in well 1281/1494 is outlined in Fig. 6.2. The coals are from a section overlain by coarse, fluvial sandstones, and seawater, moving laterally through these permeable layers, is believed to have infiltrated the seam after burial resulting in secondary sulphur enrichment (Newman, 1991). The palynology (Table 6.1) shows that an angiosperm dominated flora existed throughout deposition of the seam, which is consistent with the relatively warm, sub-tropical climate of New Zealand in the Eocene (Mildenhall, 1980). Although there can be no significant maturity differences across the 10 metre thick seam, vitrinite reflectance varies from 0.56 % - 0.72 % R_o due to increasing suppression towards the top (Table 1.2; Norgate, 1995 and references therein).

Depth (m)

Kaiata Fm. Marine Mudstone

219.1

Bioturbated medium to coarse sandstones

224.1

Lacustrine sequence: Interbedded coals and mudstones

Channel deposits: Very coarse sandstones, conglomerates

227.3

Channel margin sequence: Fine to medium sandstone, mudstone laminate, siltstone and mudstone

Lateral seawater infiltration through permeable beds

250.7

Channel deposits: Very coarse sandstone, conglomerates

255.6

Vertical infiltration of topmost coal layers

Coal

265.4

Mudstone, fine sandstone, sandy mudstone

Basement, Greenland Group metasediment

Figure 6.2 Simplified stratigraphy of the Upper Waimangaroa sector, Buller Coalfield as observed in drillhole 1281/1494. Based on information provided by Coal Research Limited, New Zealand (Dr. J. Newman). The coals are of Eocene (Bortonian) age.

Table 6.1 Pollen and spore palynology of "top" and "bottom" Buller coals.

	Top (255.6 - 255.9 m) %	Bottom (264.7 - 265.4 m) %
Angiosperm classes		
Proteaceae	2	8
Myrtaceae	11	11
H. Harissi	8	9
other triorate	3	2
Tricolpate (i.e. Tricolpites sp.)	46	23
Tricolporate	13	12
Monosulcate	2	6
Unknown	12	17
Total angiosperms	97	88
Total gymnosperms	trace	1
Pteridophyte spores	3	11

This reflectance suppression is associated with the increasingly perhydrous nature of the vitrinite (Rock Eval HI values, Table 2.2) and/or the organic sulphur content (Curry et al., 1995).

A single core of marginally mature Miocene-age coal was obtained from the Maniguin-2 well, Maniguin Island, the Philippines. This sample is referred to hereafter as the "Maniguin coal" (Table 2.2). Palynological examination revealed (in order of decreasing abundance) large cuticular fragments of unknown plant affinity, fungal remains, fern spores and angiosperm pollen. The major maceral is vitrinite. The high abundance of fungal palynomorphs suggests a senescent environment of deposition and although neither marine nor freshwater palynomorphs were visible there is abundant geochemical evidence for a major contribution from freshwater algae. For example, 4-methyl steranes are more abundant than their desmethyl counterparts in the bitumen and C_{34} botryococcanes derived from *Botryococcus* algae are present. These compounds are also abundant in the lacustrine claystone which overlies the coal and into which it grades conformably (Australian Geological Survey Organisation, unpublished results). Hence the coal may represent a senescent swamp drowned by development of a freshwater lake. The pristane/phytane ratio of the bitumen (4.0) although relatively low for a marginally mature coal, increases to 7.2 upon artificial maturation. Based on pyrolysis-GCMS analysis (Australian Geological Survey organisation unpublished results; Tegelaar and Noble, 1994) the kerogen is oil-prone and consists of a mixture of freshwater-algal and lignin-rich/vitrinitic organic matter. The sulphur content is low (0.6%) and there is no evidence in the sedimentology, palynology or geochemistry for a significant marine influence during or after deposition.

Cuttings of coals and marine shales from the GK well, South Sumatra Basin are of Oligocene-Miocene age. These are the same samples used to develop and test bicadinane maturity indicators (chapter five and Sosrowidjojo et al. 1994). A description of the stratigraphy and geological

setting is given in chapter five and further details in de Coster (1974). The depositional environment changes downwell from marine, through shallow marine/paralic to lower delta plain. Although lacustrine algae have contributed organic matter to some oils and sediments from the South Sumatra Basin (Suseno et al., 1992) there is no evidence of a freshwater algal contribution to the samples studied here. Only the deepest coals have entered the oil window and the zone of peak oil generation is not penetrated by the GK well.

6.3   Analytical protocol

Saturated and aromatic hydrocarbon fractions of the sediment extracts were analysed by gas chromatography and gas-chromatography-mass-spectrometry in the metastable reaction monitoring (MRM), selected ion monitoring (SIM) or full scan modes. Details of these analyses are given in chapter two. The definition and derivation of parameters used to monitor the fate of oleanoids are given in Table 6.2.

6.4   Results and Discussion

6.4.1 Relationship between marine influence during early diagenesis and oleananes in Tertiary coals

The coals of the Buller Basin, New Zealand arise from an angiosperm dominated flora (Table 6.1) and their bitumens contain oleanane and other plant-derived triterpanes. The abundance of these compounds is not uniform however and varies both laterally and vertically across the field (Norgate, 1995). The distribution of C_{30} triterpanes in "top" and "bottom" samples from the 1281/1494 drillhole is shown in Fig. 6.3. Also included is a chromatogram for the McKee oil which is thought to have been generated by stratigraphically equivalent coals and carbonaceous shales in the Taranaki Basin (Killops et al. 1994b)

Table 6.2   Definition and derivation of parameters used to monitor the fate of oleanoids.

Parameter	Definition	Measured from
Pr/Ph	Ratio of pristane to phytane peak area	Gas chromatogram of saturates
C_{27}/C_{29} steranes	Peak area ratio of total $\alpha\beta\beta$ and $\alpha\alpha\alpha$ isomers for C_{27} desmethyl steranes to the same isomers for the C_{29} desmethyl steranes	MRM-GCMS of saturates or branched/cyclic fraction: m/z 372→217 and 400→217 mass chromatograms
Homohopane Index	Peak area ratio of C_{35} homohopanes/(sum of C_{31}-C_{35} homohopanes), as %	SIM-GCMS of saturates or branched/cyclic fraction, m/z 191 mass chromatogram
DBT/Phe	Peak area ratio of dibenzothiophene to phenanthrene corrected for relative response after Hughes et al., (1995).	Mass chromatograms (m/z 184 and 178) reconstructed from full scan GCMS or by SIM-GCMS.
Olean/Hop	Peak area ratio of oleananes ($18\alpha+18\beta$) to $17\alpha,21\beta$-hopane	MRM-GCMS of saturates or branched cyclics m/z 412→191 mass chromatogram
OTs/Hop	Peak area ratio for the sum of 7 oleanoid triterpanes to $17\alpha,21\beta$-hopane	MRM-GCMS of saturates or branched cyclics m/z 412→191 mass chromatogram
OTs/Olean	Peak area ratio for the sum of seven oleanoid triterpanes to oleananes ($18\alpha+18\beta$)	MRM-GCMS of saturates or branched cyclics m/z 412→191 mass chromatogram
O'nenes/Olean	Peak area ratio of the sum of four oleanene isomers to oleananes ($18\alpha+18\beta$)	MRM-GCMS of the saturates: Oleanenes in m/z 410→218, Oleananes in m/z 412→191 mass chromatograms
Olean μg g⁻¹ TOC	Concentration of oleananes ($18\alpha+18\beta$) per unit TOC	Gas chromatograms of the Buller coal branched/cyclics and MRM-GCMS m/z 412→191 mass chromatograms - see text, Chapter 2.
Hopane μg g⁻¹ TOC % Pic of arom	Concentration of $17\alpha,21\beta$-hopane per unit TOC % peak area of the sum of octahydro-, tetrahydro- and dimethylpicenes to total area of resolved and unresolved aromatics	As above GCMS total ion chromatogram of the aromatics or reconstructed m/z 342, 324 and 306 mass chromatograms corrected to equivalent peak area in the TIC.
1,2,7 TMN/(1,2,6+1,6,7)	Peak area ratio of 1,2,7-trimethylnaphthalene to the sum of areas for 1,2,6 and 1,6,7-trimethylnaphthalenes	SIM-GCMS of the aromatics, m/z 170 mass chromatogram
1,2,5 TMN/(1,2,6+1,6,7) % DMP of Pic	As above for 1,2,5-trimethylnaphthalene Peak area of dimethylpicene of the sum of areas for octahydro-, tetrahydro- and dimethylpicenes, as %	As above GCMS total ion chromatogram of the aromatics or reconstructed m/z 306, 324 and 342 mass chromatograms corrected to equivalent peak area in the TIC
μg Pic g⁻¹ TOC Olean+OTs/Pic	Concentration of of octahydro-, tetrahydro- and dimethylpicenes per unit TOC Concentration ratio of oleanane ($18\alpha+\beta$)+seven oleanoid triterpanes to the sum of octahydro-, tetrahydro- and dimethylpicenes.	GCMS total ion chromatogram of the aromatics as described in the text. As above for numerator and denominator parameters.
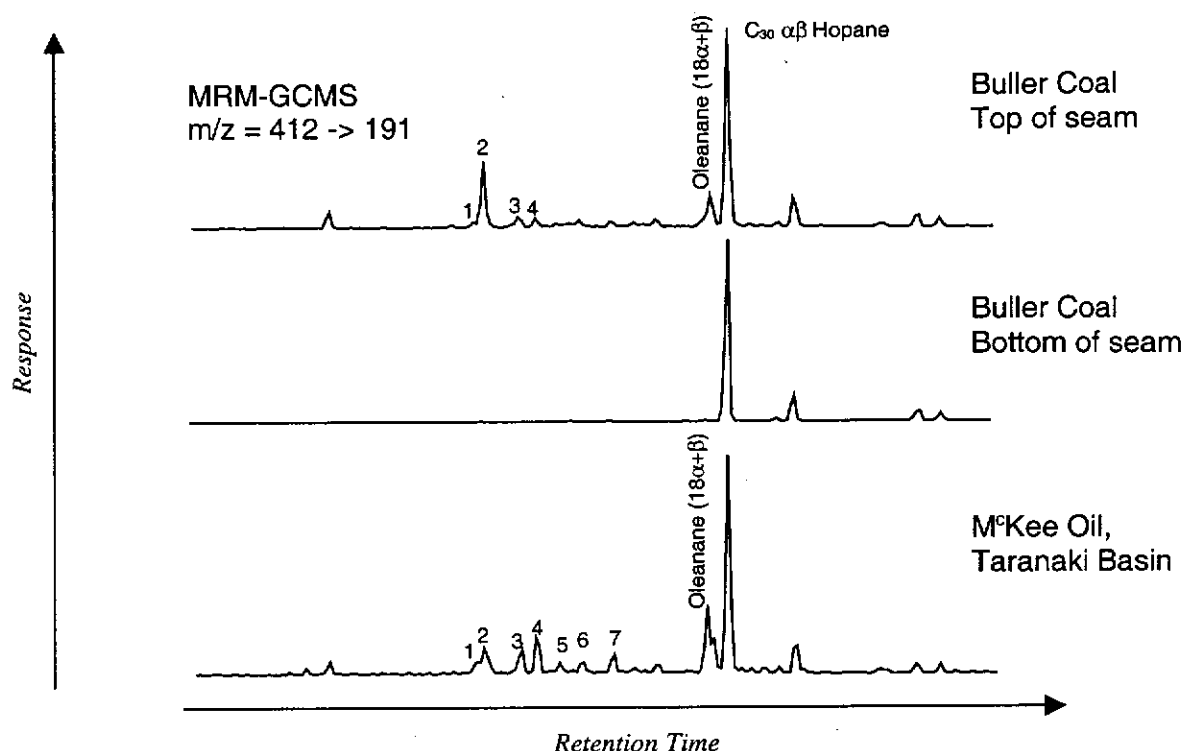
Figure 6.3   Partial MRM-GCMS chromatograms showing C_{30} triterpanes in top and bottom seam Buller coals and in the McKee-1 oil from the nearby Taranaki Basin (see Killops et al., 1994b for location). Peaks marked 1 - 7 are due to oleanoid triterpanes.

As shown in Fig. 6.3, oleananes are absent, or present at very low levels, in the bottom sample from the Buller seam. A very small peak at the retention time of oleanane, barely visible in the unexpanded chromatogram, gives a significant response in the m/z 412 → 369 chromatogram and so is probably due to lupane (Peters and Moldowan, 1993; Rullkötter et al., 1994). Correction for this minor co-elutant was not attempted. However, the true concentration of oleananes in these samples is estimated to be less than 0.5 μg g^{-1} TOC. In addition to the regular oleananes, the topmost Buller coals also contain a suite of oleanane-like triterpanes which elute before the oleananes and occur in frequent association with them. Some of these "oleanoid triterpanes" have mass spectra indistinguishable from that of 18α-oleanane while others show a small response at m/z 369 due to a pendant isopropyl group. Recently, Smith et al. (1995) identified compound 2 (Fig. 6.3) as the A-ring contracted oleanane, 5(4→3)abeo-3α(H),5β-oleanane and

the peak is thought to represent both 18α and β isomers. The identity of the other oleanoid triterpanes is unknown at present but their mass spectra, retention times and consistent co-occurrence with the A-ring contracted compounds suggest that they are also rearranged oleananes.

The mass spectrum of compound 2 (Fig. 6.4) matches well with the one presented by Smith (1995) for the synthetic 5(4→3)abeo-oleanane. The McKee oil contains relatively less of this compound than the topmost Buller Coal (Fig. 6.3). Nevertheless, A-ring contracted oleananes are more abundant in this oil than in other fluvio-deltaic oils from New Guinea and Southeast Asia (chapter three), consistent with its origin from Buller coal equivalents.
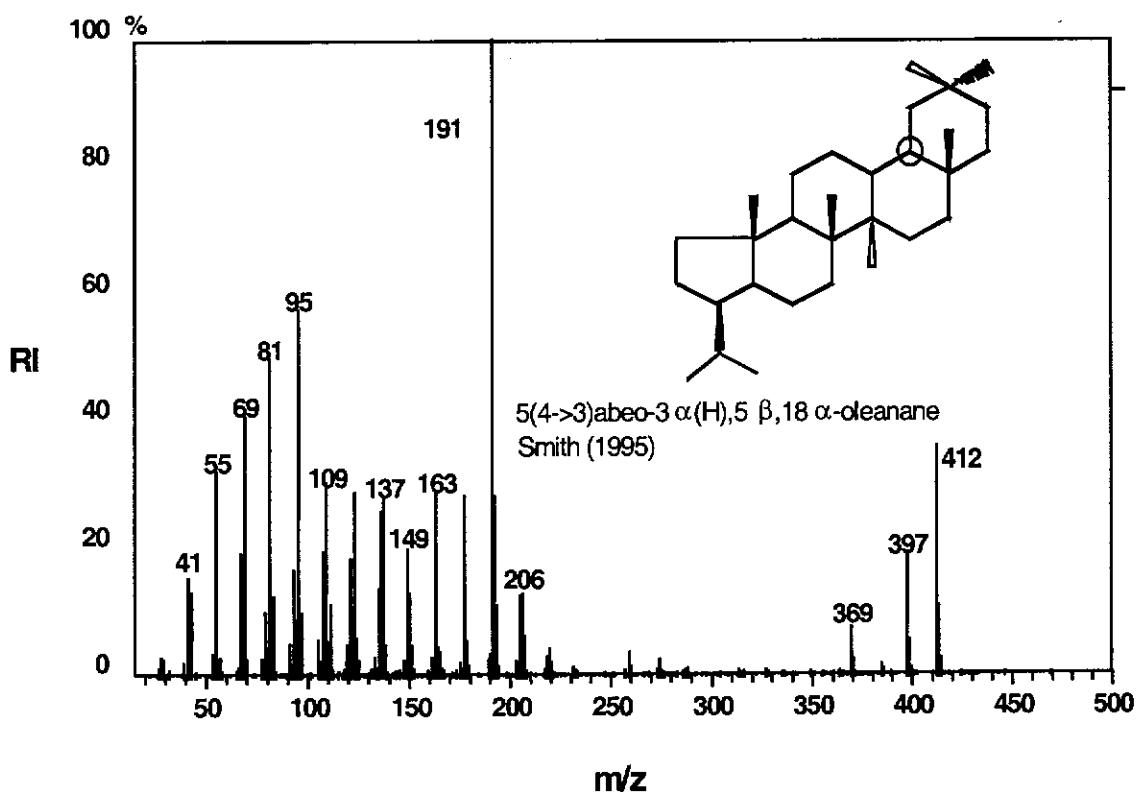

Figure 6.4   Mass spectrum of the oleanoid triterpane labelled "2" in Fig. 6.3. The spectrum matches well with the one obtained by Smith (1995) for the compound shown. RI = Relative Intensity.

Although not shown in Fig. 6.3, the Buller coals also contain A-ring degraded triterpanes such as des-A-oleananes and lupanes and the variation of these compounds with depth is similar to the ring-A intact compounds. Only traces of oleanenes could be detected by MRM-GCMS using the m/z 410→218 reaction.

The intrusion of seawater into the Buller coals cannot be inferred from the sterane distribution because the C_{27}/C_{29} sterane ratio, broadly indicative of the marine-terrestrial source balance (Peters and Moldowan, 1993), is uniformly low (Fig. 6.5A). C_{30} desmethyl steranes were not detected. The downward infiltration of sulphate-rich water is nevertheless evident from the incorporation of sulphur into the organic matter, as shown by downseam trends in total organic sulphur, dibenzothiophene/phenanthrene ratio (DBT/Phe) and the homohopane index (Figs. 6.5B-D and Hughes et al., 1995; Peters and Moldowan, 1993; Sinninghe-Damsté et al., 1995). Hydrogen index also changes downseam but this is not necessarily related to the marine infusion (J. Newman, personal communication). The down seam decrease in marine influence is accompanied by a reduction in both the absolute and relative concentration of saturated oleanoids (Fig. 6.6) and they are difficult to detect in the lowermost coals.

In contrast to the topmost Buller coals, no marine influence was present during or after deposition of the Maniguin Coal and this resulted in low values for the DBT/Phe ratio and homohopane index (0.14 and 0.63 respectively). Remarkably for Tertiary sediments of Southeast Asia, the coal contains no oleananes, oleanoid triterpanes or oleanenes (Fig. 6.7).

Although the tropical lowlands were dominated by angiosperms throughout the Tertiary (Lidgard and Crane, 1988) the possibility that an anomalous gymnosperm flora contributed to the Maniguin coal was considered. However, this is rendered unlikely by the absence of gymnosperm pollen and of conifer related diterpanes in the bitumen (Noble et al., 1985a). The lack of oleananes is not related to maturity since a) artificial maturation (sealed tube,

350 °C/72 h) failed to generate oleananes and b) the level of maturity reached is more than sufficient to generate oleananes in sediments elsewhere (e.g., Niger Delta, Ekweozor and Udo (1988); Buller coals, South Sumatra Basin, see chapter five).
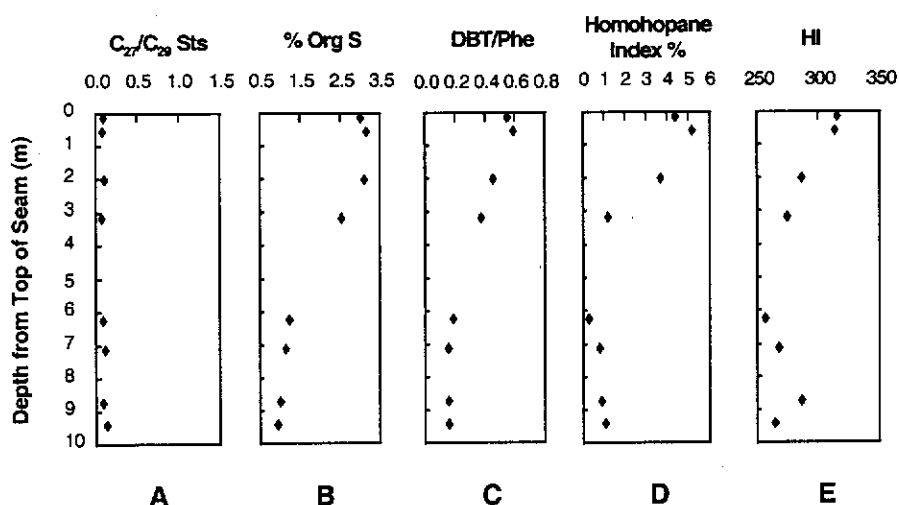
Figure 6.5 Variation through the Buller coal seam in A: C_{27}/C_{29} steranes B: % Organic sulphur C: Dibenzothiophene/phenanthrene D: Homohopane index and E: Rock Eval Hydrogen Index.
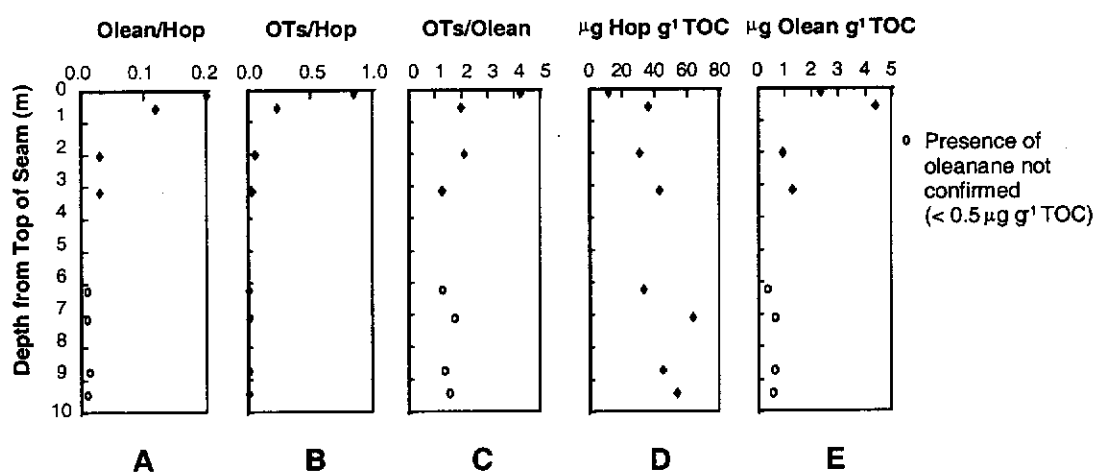
Figure 6.6 Variation through the Buller coal seam in A: Oleanane/hopane; B: Total Oleanoid Triterpanes/hopane; C: Oleanoid Triterpanes/oleanane; D and E: Concentration per unit TOC of hopane and oleanane. Open circles indicate samples for which oleanane concentration is too low for confirmation by full-scan mass spectrometry: peak areas for these samples include a non-oleanoid co-elutant.
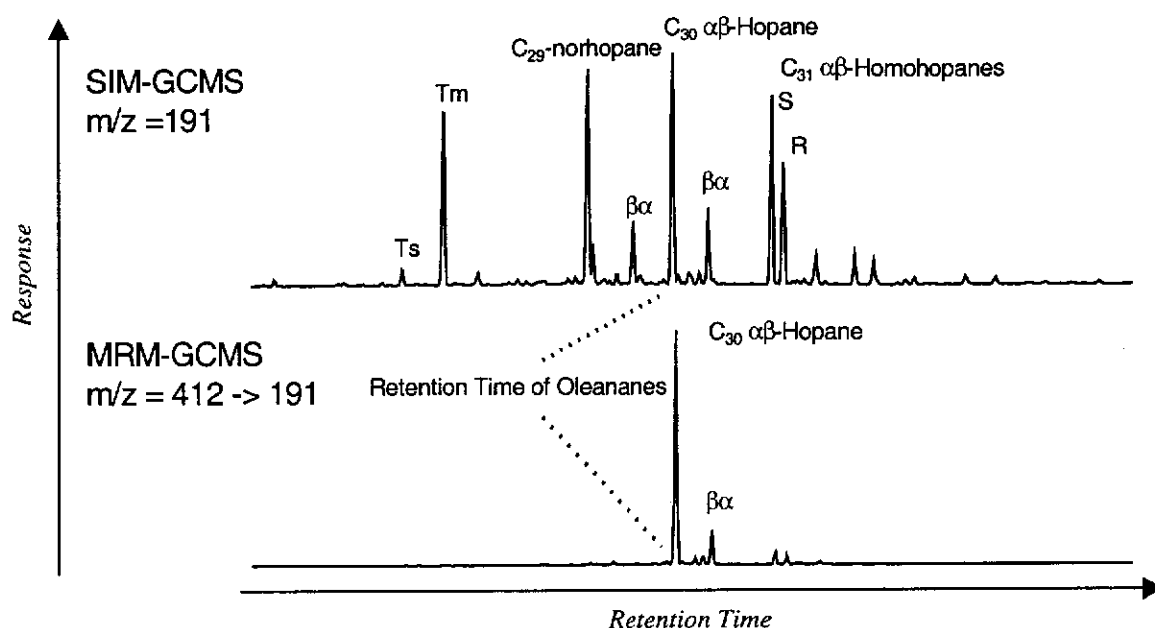
Figure 6.7   Partial selected ion monitoring (SIM) and metastable reaction monitoring (MRM) GCMS chromatograms of saturate hydrocarbons in the Maniguin coal.

The absence of saturated oleanoids in the lower Buller and Maniguin coals is probably due to efficient aromatisation and/or rearrangement of the precursors. All of the coals contain abundant aromatic compounds related to land plant precursors and specifically the oleanane skeleton (Fig. 6.8). These include octahydropicenes (OHPs), tetrahydropicenes (THPs), dimethylpicenes (DMPs) and products of ring-C cleavage such as 1,2,7 and 1,2,5-trimethylnaphthalene (Strachan et al., 1988). The most abundant monoaromatics in the Maniguin coal are the tetralin structurally related to 1,2,5-trimethylnaphthalene and an unidentified C_9 benzene. Isohexyl monoaromatic hydrocarbons of the kind identified by Ellis et al. (1996) and formed by aromatisation-rearrangement of C_{10}-methylated terpenoids are also present. Partially and fully aromatised picenes make up ca. 1.6 % of the chromatographically-resolved Maniguin coal aromatics based on peak areas in the total ion chromatogram. Their presence as major components of the bitumen, together with the absence of oleananes in this sample, signals unusually complete aromatisation of oleanenes during early diagenesis. Although low oleanane/hopane ratios are not unusual for non-marine

sediments and oils of Tertiary age (e.g. Green River Fm.: Horsfield et al.,
1994; Central Sumatra Basin: chapter three) it is exceptional for oleanane to
be undetectable - even by sensitive MRM-GCMS methods - in such samples.
In contrast, oleananes are almost universally present in Tertiary-age marine
and fluvio-deltaic samples from Southeast Asia (Robinson, 1987).
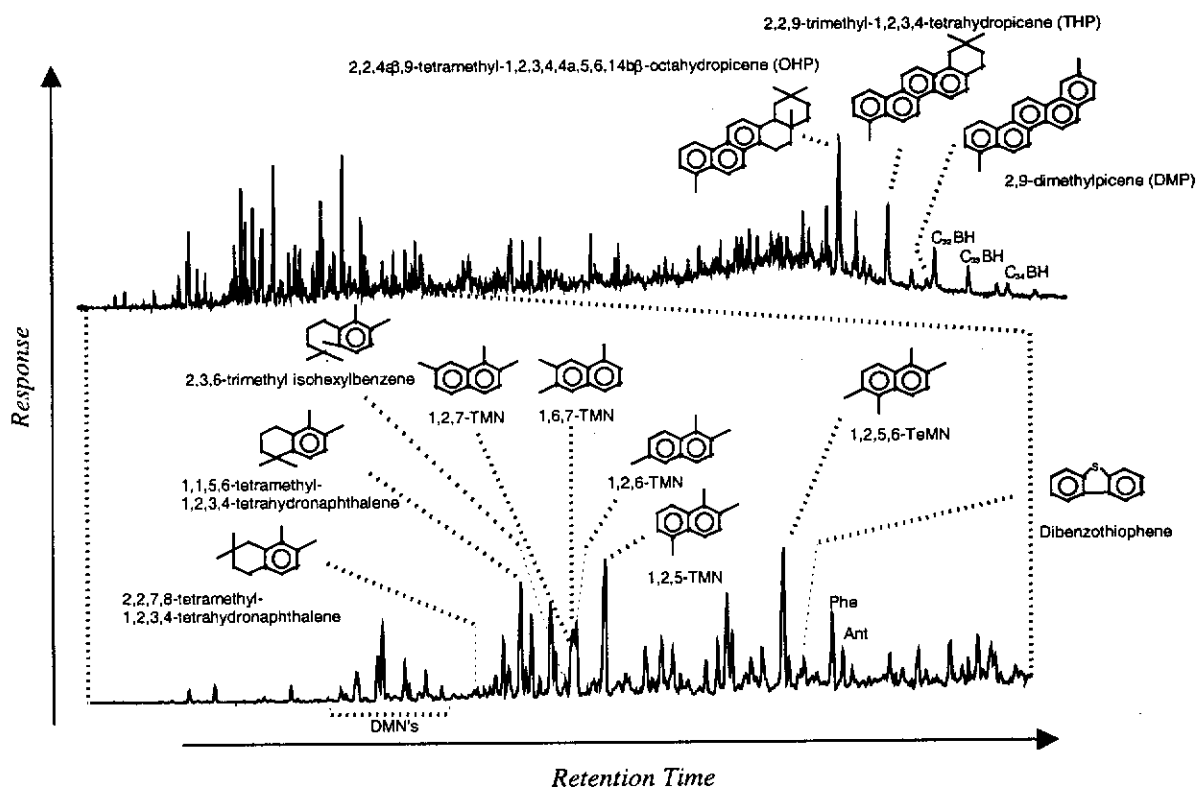
Figure 6.8   Full-scan GCMS total ion chromatogram of the Maniguin coal aromatics.
Peak identifications are based on comparison of retention times and mass
spectra with literature data (Chaffee and Johns, 1983; Chaffee and Fookes,
1988; Strachan et al., 1988 and references therein; Forster et al. 1989; Stout
1992; Ellis et al., 1996). DMN = dimethylnaphthalenes, TMN =
trimethylnaphthalenes, TeMN = tetramethylnaphthalenes, Phe =
phenanthrene, Ant = anthracene, BH = benzohopanes.

The concentration of picenes in the Buller coals ranges from 300 to ca. 1000
μg g^{-1} (Fig. 6.9A) and there is no clear down seam trend. However, since the
concentration of picenes is two to three orders of magnitude higher than that
of the oleananes (Fig. 6.6E), any change in their abundance due to the

marine influence would be minor and easily overwhelmed by other factors, e.g., minor changes in the angiosperm/gymnosperm balance (Table 6.1). A more sensitive indicator of the progressive aromatisation of the oleanane skeleton is the proportion of the fully aromatised picenes (DMPs) relative to their partially aromatised octa- and tetrahydro- counterparts (OHPs and THPs). As discussed later, this ratio is sensitive to thermal maturity but for the essentially isorank Buller coals the slight down seam increase in % DMP (Fig. 6.9D) must reflect increasing *diagenetic* aromatisation towards the bottom of the seam. The absence of oleananes in the lower samples could thus be due to more efficient operation of the progressive aromatisation pathway. In contrast, the downseam trends in 1,2,7- and 1,2,5-TMN relative to non-source specific naphthalenes (Fig. 6.9B and C) do not suggest a major role for ring-C cleavage in removing oleananes from the lower samples. The ratio of total saturated oleanoids to picenes (Fig. 6.9E) is strongly correlated with the homohopane index (Fig. 6.10) and with the inferred degree of marine influence.
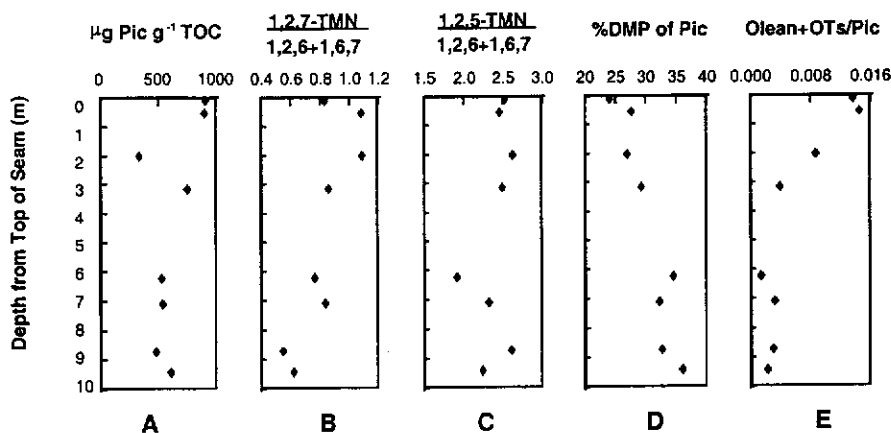
Figure 6.9   Variation through the Buller coal seam in A: Concentration of total picenes per unit TOC B: 1,2,7-trimethylnaphthalene/(1,2,6+1,6,7-trimethylnaphthalene) C: 1,2,5-trimethylnaphthalene/(1,2,6+1,6,7-trimethylnaphthalene) D: % Dimethylpicene of total picenes (%DMP/(OHP+THP+DMP)) and E: Sum of oleanoid triterpanes+oleanane/total picenes (ratio of concentrations per unit TOC).
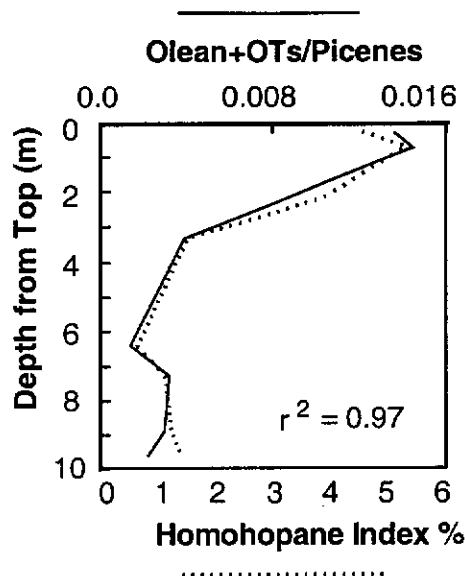
Figure 6.10   Correlation between saturated/aromatic oleanoid ratio (oleanane + oleanoid triterpanes/picenes) and homohopane index for the Buller coals. The homohopane index is %C_{35} homohopanes of the total C_{31}-C_{35} homohopanes.

6.4.2 The effect of marine influence on the abundance of oleanane in deltaic sediments

The shales and coals of the GK well in the South Sumatra Basin show varying proportions of marine-algal and land-plant derived organic matter as reflected in the overall organic carbon content (coal or carbonaceous marine shale), variable ratio of pristane/phytane, C_{27}/C_{29} desmethyl steranes (Fig. 6.11) and C_{30} desmethyl steranes/total steranes. Values of pristane/phytane ratio for the shales are consistent with deposition or transport of organic matter under sub-oxic or dysoxic conditions as are low values for the homohopane index and DBT/Phe ratio (Hughes et al., 1995; Sinninghe-Damsté et al., 1995). Note, however, that the homohopane index varies downwell and correlates strongly with the C_{27}/C_{29} sterane ratio (r^2= 0.89). Such a relationship would not be expected if the land plant detritus in the shales consisted solely of material transported directly to the site of deposition upon senescence. Rather, it is consistent with observations of modern deltaic systems where fresh plant material mixes with partially degraded matter initially laid down in paralic peat swamps and subsequently eroded and redeposited in marine sediments (Diessel, 1992). In this model,

increasing distance from the paleo-shoreline not only means a reduced supply of land plant matter but also a reduction in the proportion of this matter which has experienced terrestrial as opposed to marine diagenetic conditions. That is, the proximal sediments will contain a relatively larger component of reworked peat organics. Hence a correlation between indicators of depositional environment (homohopane index) and source matter type (C_{27}/C_{29} steranes) is reasonable. The dibenzothiophene /phenanthrene ratio does not show the same downwell trend (Fig. 6.11E) possibly because of the complicating effects of maturity and/or sediment lithology on this ratio (see Hughes et al., 1995).
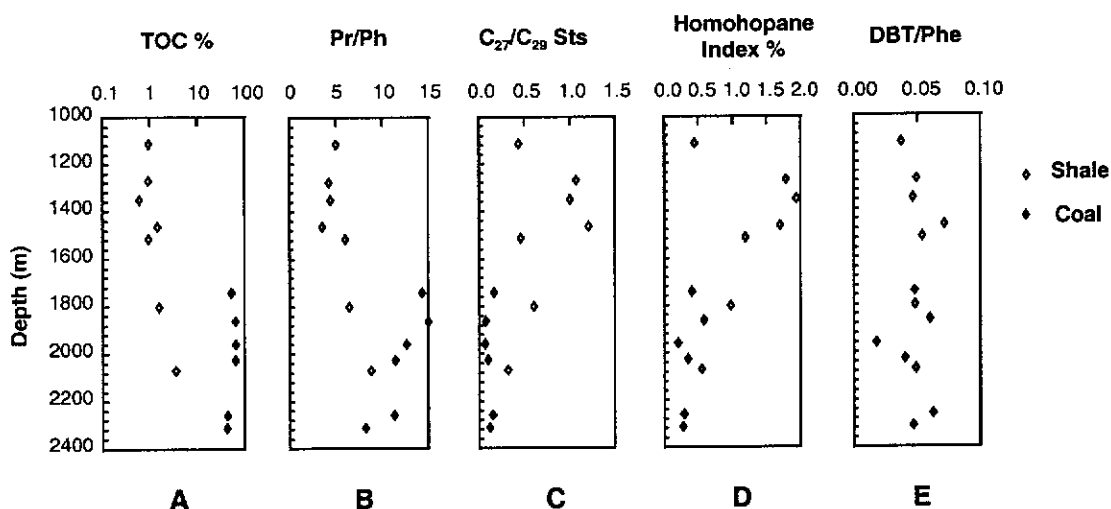
Figure 6.11 Variation down the GK well, South Sumatra Basin in A: Total Organic Carbon B: Pristane/phytane C: C27/C29 steranes D: Homohopane index and E: Dibenzothiophene/phenanthrene.

The distributions of C_{30} triterpanes in a shale from 1800 m and a coal from 1959 m are shown in Fig. 6.12. Oleanane/hopane is higher in the shale than the coal - a feature which has been observed previously for interbedded deltaic coals and shales from the Far East (Curiale and Lin, 1991). The variation in the abundance of oleananes, rearranged oleananes and oleanenes through the GK section is shown in Fig. 6.13. Oleanenes were only detected in the shallowest (least mature) samples with olean-13(18)-ene

the most abundant isomer (Fig. 6.14), as expected from stability
considerations (Rullkötter et al., 1994).

If the abundance of oleananes in deltaic systems was controlled solely by
the degree of land plant contribution, oleanane/hopane would be expected to
correlate *inversely* with indicators of marine influence in the GK sediments.
The data in Fig. 6.15 and 6.16 show that in fact the reverse is true -
oleanane/hopane is *directly* and strongly correlated with both the C_{27}/C_{29}
sterane ratio and the homohopane index. The oleanane/hopane and C_{27}/C_{29}
sterane ratios are used here, rather than absolute biomarker concentrations,
in order to normalise for the wide variation in biomarker content as a function
of maturity and TOC content. However, similar trends are evident when
absolute biomarker concentrations per unit TOC are compared (Fig. 6.17).
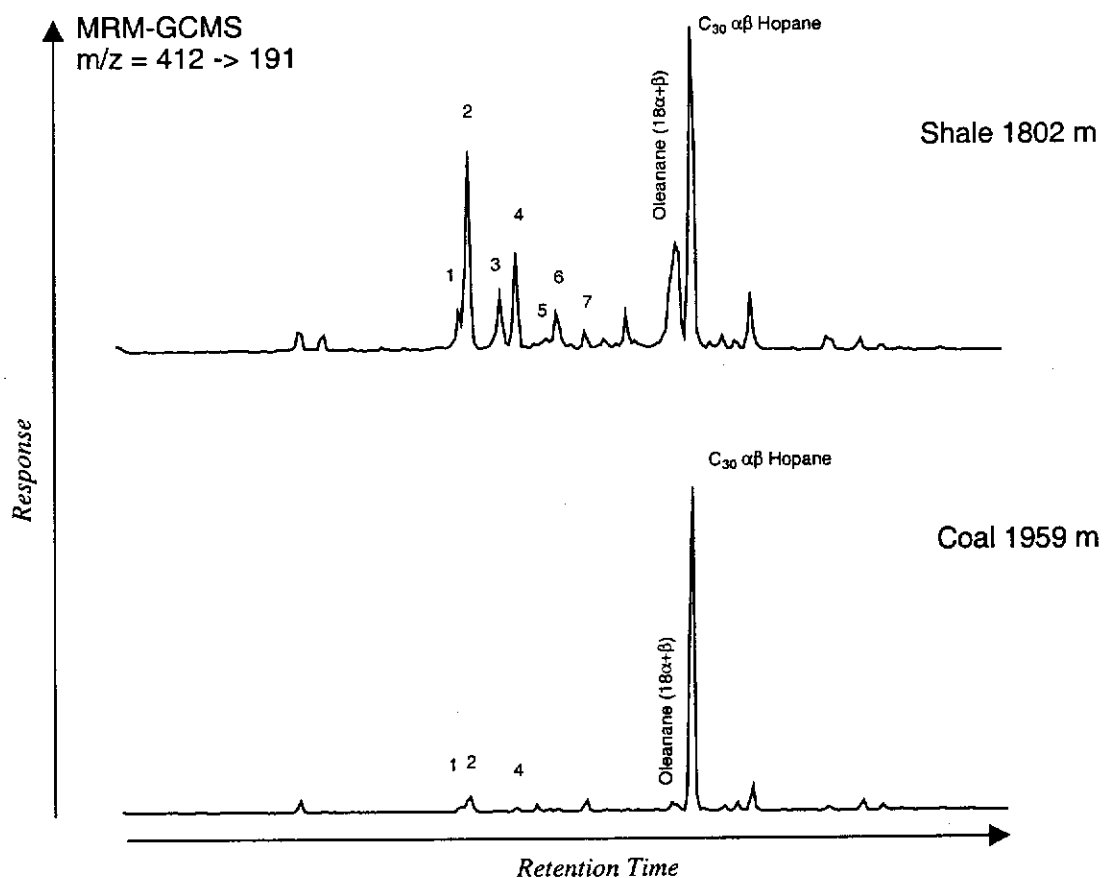
Figure 6.12 MRM-GCMS chromatograms showing the distribution of C_{30} triterpanes in a
shale and coal from the GK well. Numbers refer to oleanoid triterpanes (see
text).
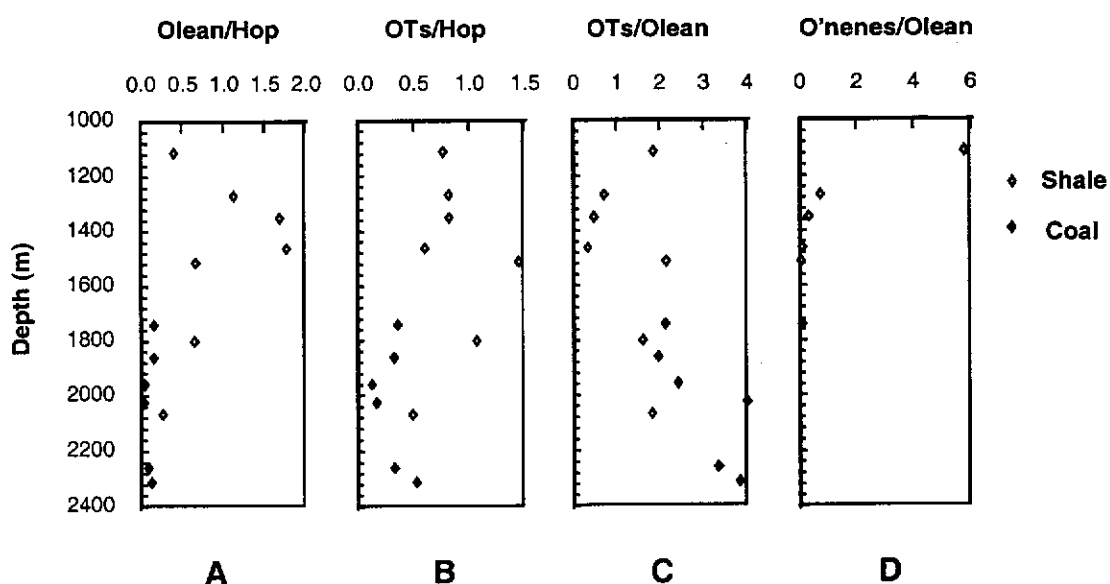
Figure 6.13 Variation down the GK well in A: Oleanane/hopane; B: Oleanoid triterpanes/hopane; C: Oleanoid triterpanes/oleanane and D: Oleanenes/oleanane.
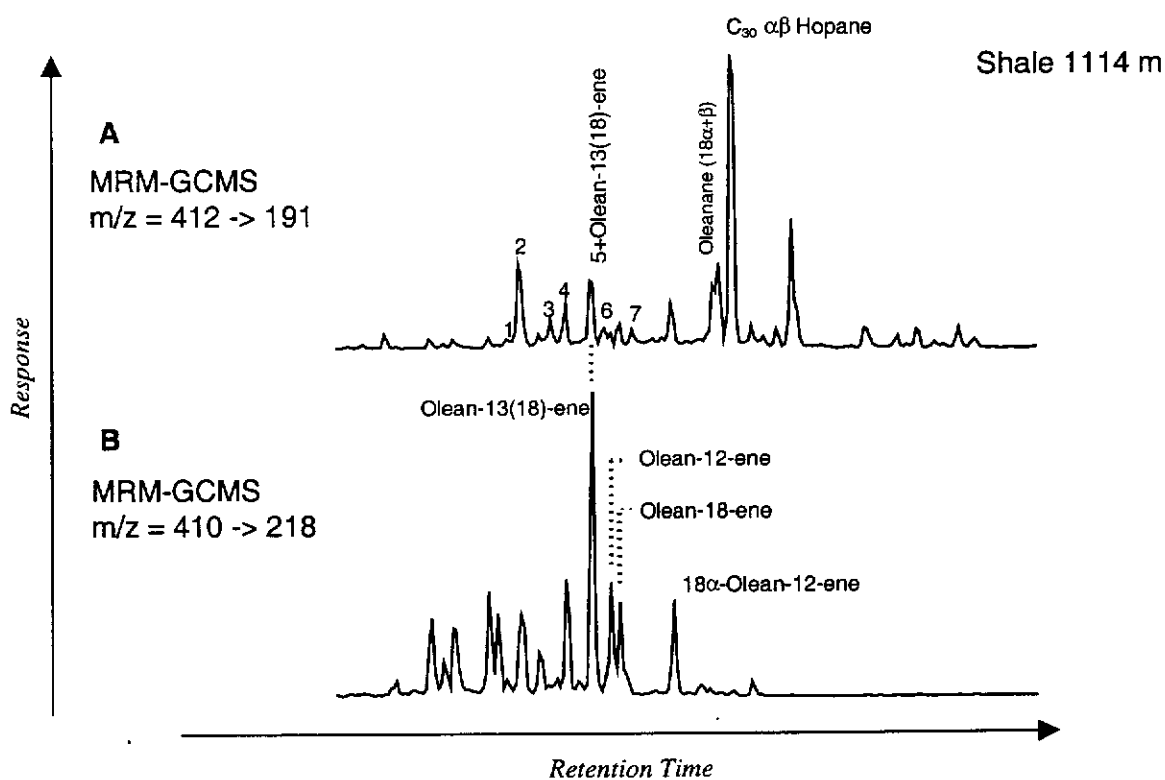
Figure 6.14 MRM-GCMS chromatograms for the saturate fraction from the least mature GK sample showing A: Saturated oleananes and hopanes B: Oleanenes (identifications based on Rullkötter et al., 1994). Numbers refer to oleanoid tritperpanes (see text).

Figure 6.15 Correlation between oleanane/hopane (Olean/Hop) and C_{27}/C_{29} steranes (C_{27}/C_{29} sts) for sediments from the GK well. See Fig. 2.1 for a generalised stratigraphy of the GK well.
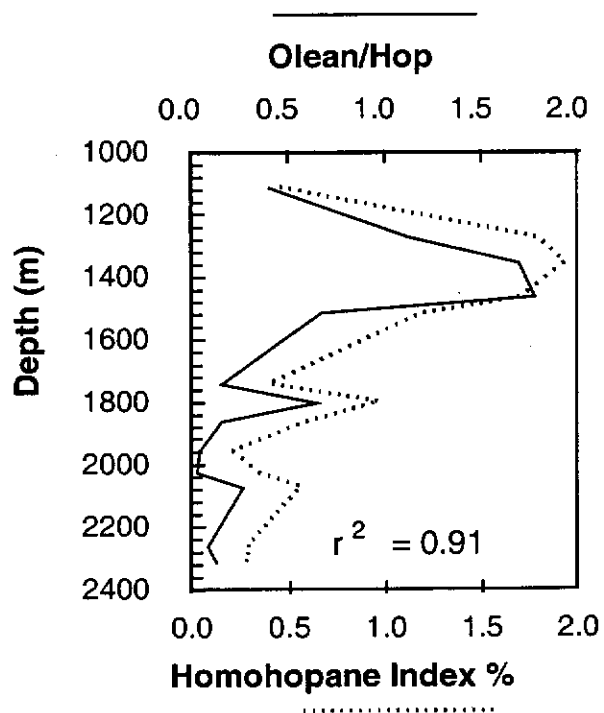
Figure 6.16 Correlation between oleanane/hopane (Olean/Hop) and homohopane index for sediments from the GK well. See Fig. 2.1 for stratigraphy of the GK well.
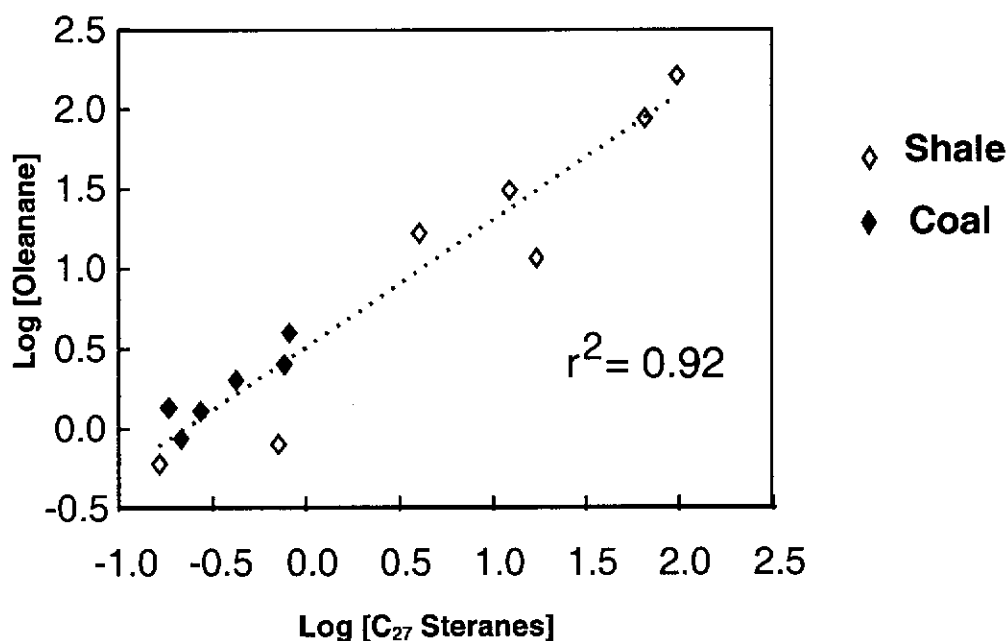
Figure 6.17   Correlation between the concentration of oleananes and total C_{27} steranes (μg g^{-1}TOC) for sediments of the GK well. Log-Log transformed data is used for ease of presentation. The correlation coefficient for the untransformed data is 0.90.

The increase in oleanane with increasing marine character depicted in Fig. 6.16 and Fig. 6.17 could be explained in two ways: a) the precursor compounds are present in certain plant organs (e.g. leaves) which are selectively and efficiently transported to the site of marine deposition, or b) a chemical or microbial effect of marine influence during early diagenesis retards the formation of aromatic derivatives and enhances the expression of the saturated compounds. However, the latter explanation is supported by the behaviour of other saturated oleanoids. As shown in Fig. 6.18, the abundance of the oleanoid triterpanes with respect to hopane increases with marine influence but their abundance *with respect to oleanane* generally decreases. This is consistent with marine depositional conditions encouraging both the expression of saturated with respect to aromatic oleanoids and of intact with respect to rearranged skeletons. It is known that A-ring contracted triterpenes, precursors to the saturated compounds, form during acid-catalysed dehydration of 3β-triterpenols (Elgamal et al., 1969)

whereas microbial dehydration leads to Δ^2 triterpenes (ten Haven et al., 1992b and references therein). The pH of tropical peat swamps is typically low, due to a lack of neutralising minerals (Given and Dickinson, 1975; Sikora and Keeney, 1983) and values between two and three are common. Thus deposition of plant matter in a peat swamp as opposed to alkaline marine sediments could enhance the formation of A-ring contracted with respect to intact oleananes (both remaining subordinate to aromatic oleanoids). The alternative selective transport hypothesis would require different transport efficiencies for the precursor lipids of the oleanoid triterpanes and the oleananes. This in turn would imply that the two groups of compounds have their origin in different plants or in different plant organs.
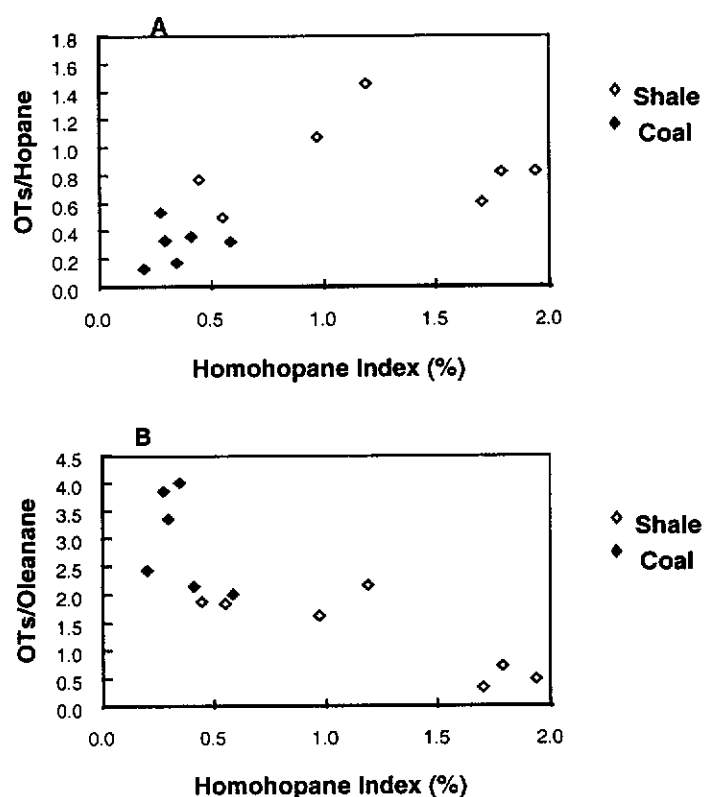
Figure 6.18 Plots showing the relationship between homohopane index and A: Oleanoid triterpanes/hopane and B: Oleanoid triterpanes/oleanane for sediments of the GK well.

Aromatic derivatives of the oleanoid skeleton such as dimethylpicenes and 1,2,7-trimethyl naphthalene (via C-ring cleavage) are less abundant in the GK samples than in the Maniguin and Buller coals (Fig. 6.19). Picenes (OHPs, THPs and DMPs) make up from 0.06 to 0.58 % of the total aromatics suggesting that aromatisation processes were less efficient overall for these samples. Furthermore, the abundance of aromatic oleanoids varies in a roughly inverse manner to that of the oleananes, the highest concentrations being found in samples with the least marine influence. Note that the trends shown in Fig. 6.19 are complicated by maturity effects because both the degree of aromatisation and that of methyl group migration increase with increasing thermal stress (Hayatsu et al., 1987; Strachan et al., 1988). This is apparent in Fig. 6.19D which shows the increasing proportion of the fully aromatised oleananes (dimethylpicenes) with respect to their partially aromatised counterparts (octa- and tetrahydropicenes) with increasing depth. The dimethylpicenes do not appear at all until ca. 2300 metres, however, which emphasises the lower degree of diagenetic aromatisation of the GK organics as compared to the Maniguin and Buller coals.
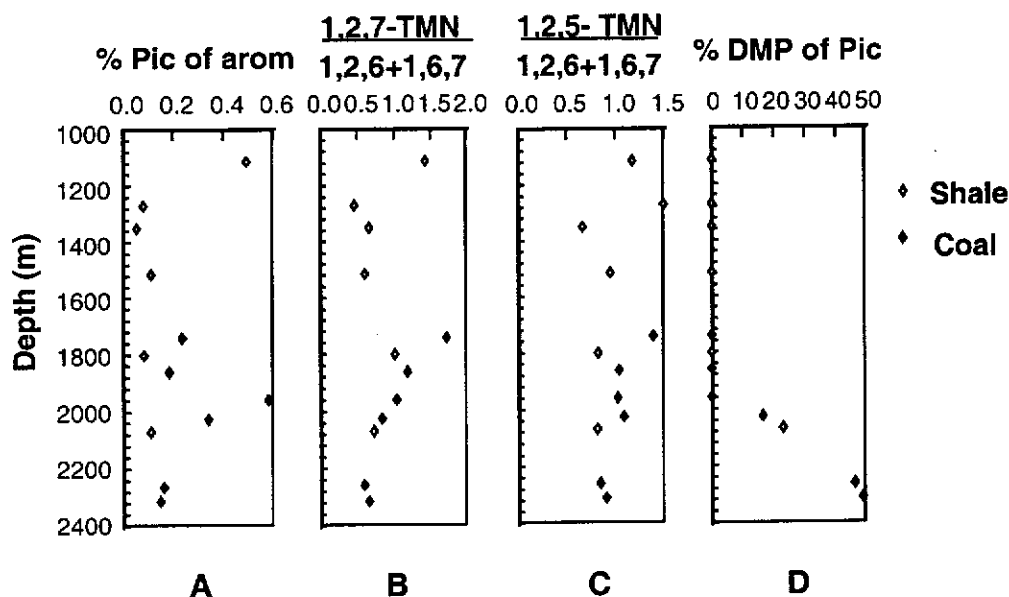
Figure 6.19 Variation down the GK well in A: % picenes (OHP+THP+DMP) of the total aromatics B: 1,2,7-trimethylnapthalene/(1,2,6+1,6,7-trimethylnaphthalene) C: 1,2,5-trimethylnaphthalene/(1,2,6-+1,6,7-trimethylnaphthalene) and D: % Dimethylpicene (% DMP/(OHP+THP+DMP)).

Ring-A degraded oleanoids, both saturated (des A oleananes, ursanes) and aromatic (octahydrochrysenes) were also identified in the GK samples (data not shown). However, in keeping with the observations of Stout (1992) for the Brandon lignite, these compounds were always subordinate to their intact counterparts and they showed similar variation with depth. This suggests that changes in the extent of A-ring degradation are not responsible for the variation in oleanane/hopane, affirming the suggestion of Stout (1992) that this pathway is incidental to progressive aromatisation and ring-C cleavage.

Summarising the results for the GK samples, contact of land plant matter with seawater during early diagenesis appears to enhance a) expression of saturated with respect to aromatic oleanoids and b) preservation of the intact with respect to A-ring contracted skeletons.

6.4.3 Mechanism of oleanane enhancement by a "marine influence"

The term "marine influence" has been used in this chapter to describe the effects of seawater on the early diagenesis of land-plant matter. Because many freshwater lakes and peat swamps are acid and low in minerals, contact with seawater will generally mean an increase in pH and in the availability of sulphate. Sediment Eh may be low or high in both marine and terrestrial systems, although some restriction on oxygen supply is presumably necessary for the accumulation of hydrogen-rich organic matter in either setting. High values of the pristane/phytane ratio are usually considered evidence of oxic deposition in fluvio-deltaic systems, but this refers only to oxygen availability in the transport and very early diagenetic stages. Most peat swamps are anoxic within a few centimetre of the surface (Given and Dickinson, 1975; Sikora and Keeney, 1983) and incorporation of reduced sulphur into the topmost Buller coals shows that these sediments were anoxic when the sea-water infusion occurred.

A variation in the extent of catalysis on the surface of clay particles cannot explain the trends seen in oleanane abundance in the Buller coals and South Sumatra Basin sediments. This is so because a) the Buller coals have a very low and essentially uniform mineral content (Norgate, 1995 and references therein), and b) oleanane abundance covaries with C_{27}/C_{29} sterane ratio and homohopane index in the South Sumatra Basin even if the shale lithologies are considered in isolation (Figs. 6.11C and D vs. Fig. 6.13A). This emphasises the fact that, in deltaic systems, host sediment lithology is a poor guide to the conditions experienced by organic matter during early diagenesis. This may be especially true in dominantly regressive settings where much redeposition of terrestrial organics in marine sediments will have occurred.

Recently, Poinsot et al. (1995) have identified a series of sulphurised higher plant triterpenes in evaporitic carbonates. The occurrence of these compounds, and the complete absence of aromatic oleanoids in the same samples led them to suggest a role for sulphur in preserving the saturated hydrocarbon skeleton. Alternatively, environmental conditions associated with the high sulphur content, such as high pH and/or a microbial community different to that found in non-evaporitic systems may have hindered aromatisation of oleanenes. The present study has shown that preservation of saturated compounds is also enhanced by normal marine conditions. Furthermore, this occurs even when the incorporation of sulphur into organic matter is relatively minor. The values of the DBT/Phe ratio of all of samples studied here are at the low end of the range reported by Hughes et al. (1995) for oils from various depositional environments and many oils with high oleanane/hopane ratios are low in organic sulphur. The role of pH in determining oleanene preservation is difficult to quantify as bulk solution pH does not necessarily relate to the reactivity of mineral surfaces or to conditions within an organic matrix. However, one reaction known to be catalysed by acid in vitro - the formation of A-ring contracted oleananes - is apparently suppressed under marine conditions. Furthermore, given that many aromatisation reactions are thought to be microbially mediated, pH

could affect oleanene preservation indirectly by altering the composition of the microbial community.

6.4.4 Implications for petroleum geochemistry

The change in the abundance of oleananes through the Buller Seam has important implications for oil-source correlation in the nearby Taranaki Basin and for fluvio-deltaic systems generally. Killops et al. (1994b,1995) used the abundance of oleanoid/ursanoid triterpanes relative to diterpanes to infer paleofloral input and age for oils from the Taranaki Basin, making use of an "angiosperm/gymnosperm index" or "AGI". It is not possible to calculate this index for the Buller coals because their diterpane distribution differs from samples in the Taranaki Basin (e.g., fichtelite, the saturated analog of retene, is not included in the AGI but is abundant in some Buller coals; Norgate, 1995). However, an oil generated from coals like those near the bottom of the Eocene Buller section (Hydrogen Index = 287, Fig. 6.5E) would contain various diterpanes but no oleananes and hence could easily be mis-attributed to a pre-Tertiary source. Furthermore, diagnostic aromatic oleanoids such as specific picene isomers and 1,2,7-trimethylnaphthalene would not necessarily appear in such an oil. Loss and rearrangement of alkyl substituents at high maturity tends to obscure source related isomer distributions (Strachan et al., 1988; Yong-Ge et al., 1995).

The results of this study suggest that marine infusion of coals during early diagenesis increases the oleanane/hopane ratio of their bitumens. If wider studies show this to be a general phenomenon, it may resolve a long-standing difficulty in oil-source correlation for terrigenous oils. Fluvio-deltaic oils from Tertiary basins nearly always show abundant higher plant triterpanes (Ekweozor and Udo, 1988; McCaffrey et al., 1994; Noble et al., 1991; Robinson, 1987) and sometimes correlate better in this respect with proximal shales than with flood-plain coals. Yet, the shales may not contain enough oil-prone organic matter to account for the volume of petroleum

generated (Noble et al., 1991; L. ten Haven, personal communication). In a sequence stratigraphic study of coals, Curry et al. (1995) concluded that the lowstand to earliest transgressive coals were the most oil-prone and also the most likely to be affected by epigenetic marine influence. Preferential generation from these facies, which may not always be well represented in sampling programs, could explain the high oleanane/hopane ratios of oils derived from Tertiary-age coals. Alternatively (or additionally) the same coarse-grained sediments which allow access of seawater to coal/peat beds during early diagenesis could act as the most efficient expulsion/migration routes for hydrocarbons leaving the coal bed. Again, the chemistry of the resultant oils would reflect that of the marine-influenced coals. Several fluvio-deltaic oils of the Taranaki Basin contain sulphur with a "marine" isotope signature (Hirner and Robinson, 1989).

As discussed above, the abundance of oleanane increases, rather than decreases, with distance from the paleoshoreline in the South Sumatra Basin. Conversely, the abundance of A-ring contracted oleananes and other "oleanoid triterpanes" relative to intact oleananes decreases with increasing marine influence. Taken together, these observations might provide a means of distinguishing between source rocks laid down in flood-plain, paralic and marine deltaic settings, based on the oil chemistry alone (Fig. 6.20). That is, we would expect a Tertiary-age deltaic oil with a) low concentrations of both oleanane and oleanoid triterpanes to have originated from non marine-influenced coals or lacustrine sediments; b) high concentrations of both oleanoid triterpanes and intact oleananes from marine influenced coals and/or marine sediments containing reworked peat organics, and c) abundant oleanane but low oleanoid triterpanes from marine sediments containing less reworked plant organic matter and perhaps further away from coastal swamps. Because factors other than depositional environment can affect the abundance of oleananes and oleanoid triterpanes, these concepts can only be tested using a very large and internally consistent data-set. For oleanane/hopane at least, such a data-set has been generated by Geomark Research Inc. (C. Shiefelbein, personal communication) and this company

kindly provided oleanane/hopane peak height ratios for 271 Tertiary-age oils from Asia and Australasia. For commercial reasons, individual oils cannot be identified but the data-set was filtered to remove oils which had been biodegraded or for which the age of the source rocks was uncertain. The oils were then sorted into three groups based on the dominant organic matter type contributing to the source, i.e., "fluvio-deltaic" (land-plants), "lacustrine" (freshwater algae) and "marine" (marine algae). This classification relies on a combination of biomarker and isotope criteria such as pristane/phytane ratio, distribution of C_{27}:C_{28}:C_{29} steranes, presence or absence of 4-methylsteranes, dinosteranes, cheilanthanes etc. The relative abundance of oleananes was not used in classifying the oils but all have some contribution from angiosperm organic matter. The "fluvio-deltaic" group (143 oils) come from the Ardjuna, Taranaki, Kutei (Mahakham Delta) and Baram Delta (offshore Brunei and Sarawak) basins. These basins were sub-classified according to the style of source rock development, i.e., whether the source interval was laid down under a more transgressive or regressive regime. The asssesment is based on the published stratigraphy (Czochanska et al., 1988; Diessel, 1992 and references therein; Ellenor, 1984; Hoffmann et al., 1984; Killops et al., 1994b; Noble et al., 1991) and bears on the likelihood of land-plant detritus being deposited in marine as opposed to terrestrial sediments. The former is more likely in regressive delta systems where falling sea level leads to peneplanation and down-cutting of coastal peat deposits (Diessel, 1992).

A comparison of the median oleanane/hopane ratios for fluvio-deltaic, lacustrine and marine oils is shown in Fig. 6.21. In keeping with the improved preservation of oleananes under marine conditions, oleanane/hopane is only slightly lower for oils derived mainly from marine organic matter than for those derived mainly from land-plants. Furthermore, the oleanane/hopane ratio is far lower for oils derived from lacustrine settings, even though the source rocks for such oils might be expected to contain a similar or higher proportion of land-plant debris as those of the marine oils.
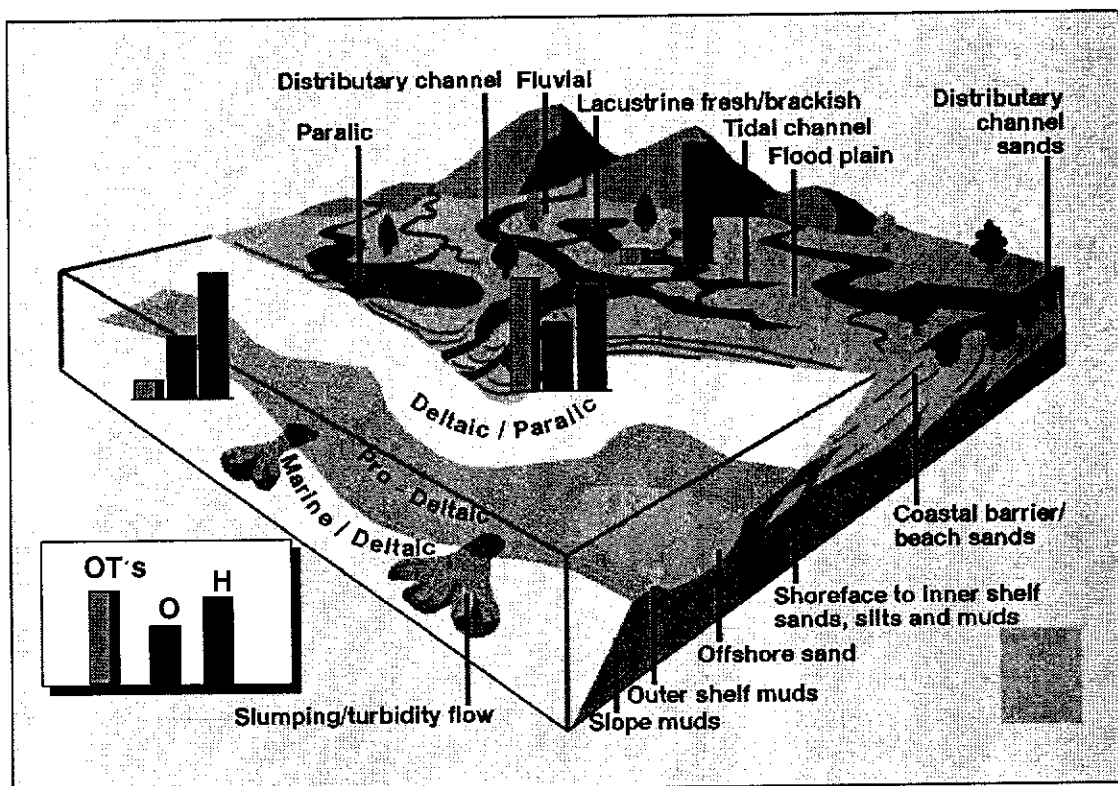
Figure 6.20 Triterpenoid patterns expected for source rocks in different parts of a deltaic system. See the text for further explanation.

A comparison of the median oleanane/hopane ratio for fluvio-deltaic oils from the Ardjuna, Taranaki, Kutei and Baram Delta Basins is shown in Fig. 6.22. As can be seen, the highest values are obtained for oils from deltaic source rocks laid down under regressive conditions. Conversely, oils from source rocks deposited under transgressive conditions, such as most from the Ardjuna Basin, show the lower oleanane/hopane ratios typical of in-place floodplain coals. Again, these data emphasise the role of depositional environment, not just organic matter type, in determining the oleanane/hopane ratio.

6.5   Conclusions

The abundance of oleananes and rearranged oleananes in sediments from New Zealand, the Philippines and Indonesia is directly correlated with the extent of diagenetic marine influence and inversely correlated with the degree of oleanoid aromatisation.
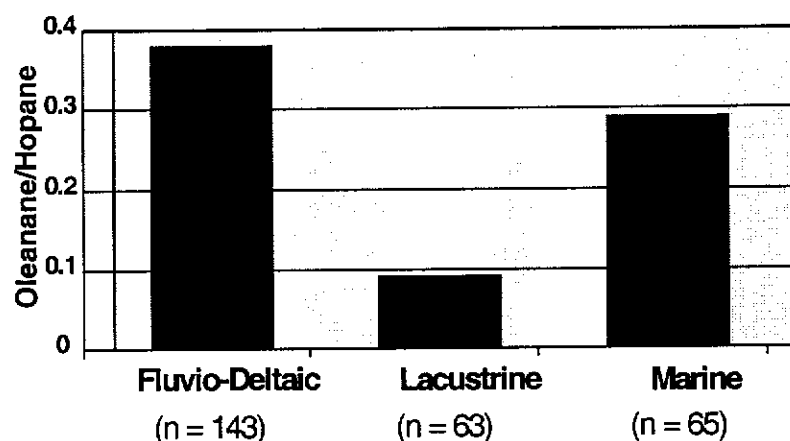
Figure 6.21   Median oleanane/hopane ratio for 271 Tertiary-age oils from Indonesia, Thailand, Malaysia, Japan, Taiwan, Vietnam, Myanmar, Philippines and New Zealand. Data courtesy of GEOMARK RESEARCH, INC.The terms "fluvio-deltaic", "lacustrine" and "marine" refer to the primary organic matter type giving rise to the oils, i.e, land plants, lacustrine algae and marine algae respectively.
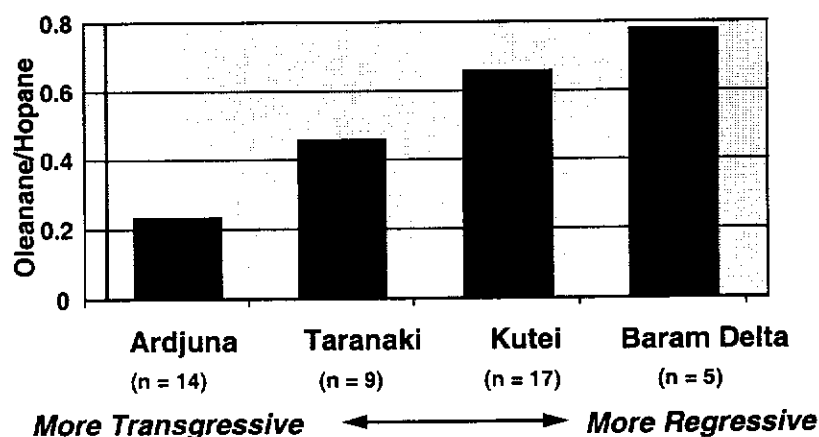
Figure 6.22   Median oleanane/hopane for fluvio-deltaic oils from four basins in Indonesia, North Borneo and New Zealand showing differing degrees of transgressive and regressive influence in source rock development.

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This indicates that the occurrence of oleananes in a mature sediment or oil is enhanced by contact with seawater during early diagenesis. This may occur through redeposition of land plant matter in marine sediments or *in-situ* by secondary seawater infiltration of a coal or peat. Where no marine influence occurs, it is possible for aromatisation or rearrangement of precursor lipids to proceed to the point where no saturated oleanoids appear in the bitumen. Although the concentration of A-ring contracted oleananes with respect to aromatic oleanoids increases with increasing marine influence, their abundance relative to oleananes decreases. This is in keeping with laboratory experiments suggesting that A-ring rearrangment is enhanced by acid conditions.

From the present study it is not possible to determine which aspect of a marine influence - pH, Eh or an altered microbial regime - is critical to the expression of oleananes. Sulphur sequestration, if an important preservation mechanism, is accompanied by only minor incorporation of sulphur into the bulk organic matter. Nevertheless, only very small amounts of sulphur would be required to bind and protect oleanenes from aromatisation. Whatever the underlying cause, the enhancement of oleanane expression by a marine influence has important implications for source rock location and resource assessment in deltaic petroleum systems. Although further studies are needed, one may speculate that a Tertiary-age, deltaic crude oil a) with low concentrations of both oleanane and A-ring contracted oleananes has originated from non-marine influenced coals or lacustrine sediments b) with high concentrations of both A-ring contracted and intact oleananes from marine influenced coals and/or marine sediments containing reworked peat organics, and c) with abundant oleanane but low A-ring contracted oleananes from marine sediments containing less reworked plant organic matter and perhaps further away from coastal swamps.

CHAPTER 7:   CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1   Introduction

As stated in chapter one, the purpose of this study was to assist oil-oil and oil-source correlation and to gain insight into the conditions needed for development of oil-prone sediments. More specifically, the aim was improve understanding of the factors controlling the occurrence, relative abundance and carbon isotope composition of land-plant derived compounds in oils.

7.2   Conclusions

The conclusions from this study can be summarised under four headings:

1.   Factors determining the shape and position of n-alkane isotope profiles (chapters three and four)

2.   Factors determining the carbon isotope composition of plant resins and resin derived compounds in oils (chapter four)

3.   Factors controlling the distribution and relative abundance of polycadinene-related compounds (chapters three and five)

4.   Factors controlling the distribution and relative abundance of oleanoid compounds (chapters three and six)

7.2.1   Factors determining the shape and position of n-alkane isotope profiles

As discussed in chapters five and six, the concentration of oleananes and bicadinanes cannot reliably be used to estimate the degree of terrigenous

influence on the source of an oil because of strong diagenetic and maturity control on the abundance of these compounds. However, the carbon isotope composition of *individual* n-alkanes in oil appears to be largely immune to early diagenetic conditions and to maturity, at least in the C_{12} - C_{34} range Thus n-alkane isotope profiles make an excellent source correlation tool. Negatively sloping profiles appear to be characteristic of oils generated from higher plant matter, with marine and lacustrine oils more commonly showing flat or positively sloping profiles. The most likely explanation for the negative sloping profiles for fluvio-deltaic oils and sediments is the slight ^{13}C enrichment that accompanies the incorporation of the plant biomass into bacterial membrane lipids. A slight isotopic anomaly at n-C_{17} for FD oils correlates with the concentration of algal-related steranes and may indicate a minor marine contribution to the source. However, other molecular indicators of a marine input, such as the the C_{30} sterane index, are not sensitive enough to confim the origin of this anomaly. Because n-alkane isotope profiles are not affected by early diagenetic or secondary influences in the manner of some biomarker ratios, they are useful when doubts arise as to whether trace biomarker components accurately reflect the character of the bulk oil and its source. This is particularly so in deltaic petroleum systems where migration contamination and migration fractionation phenomema are more common than in other systems. Conifer plants produce n-alkanes which are slightly but systematically enriched in ^{13}C with respect to those from angiosperms. Although the available database is small, these differences also manifest themselves in the carbon isotope composition of whole oils derived respectively from conifer and angiosperm organic matter.

Biomarker and n-alkane isotope profiles are best used in a complementary manner. Biomarker profiles provide valuable information about the types of organic matter which contributed to the oil and (in some cases) its age. They also provide information about the lithology of the source rock and, taking account of the information in chapter six, may provide a subtle indication of the nature of the depositional enviroment. n-Alkane isotope profiles act as excellent oil-source and oil-oil correlation tools andare effective even at high

levels of biodegradation and across a wide range of depositional environments. Since the shorter chain n-alkanes are the first to be lost during weathering, water washing and biodegradation, the first effect of these phenomenah on a fluvio-deltaic oil will be to shift the bulk $\delta^{13}C$ value towards lighter (more negative values). However, further degradation, involving complete depletion of the n-alkanes will reverse this trend, causing a shift towards heavier values for the residual oil. Lack of appreciation of this behaviour - which would be less complex for marine and lacustrine oils - could confound oil-source correlations based on bulk oil $\delta^{13}C$ values.

7.2.2. Factors determining the carbon isotope composition of plant resins and resin derived compounds in oils

This study has shown that a) conifer (Type I) resins and their catagenetic products in oils and sediments are isotopically heavy compared with angiosperm (Type II) resins and their products, and b) extant plant resins are isotopically light compared with their fossil counterparts. Both resins and resinites are isotopically heavier than other plant lipids in coals and oils. The reasons for the carbon isotope difference between conifer and angiosperm resins are reasonably well understood and are discussed in chapter four. However, insufficient data exists to distinguish between the several possible reasons for the difference in average $\delta^{13}C$ for resins and resinites. Resin derived compounds in oils and sediments, especially those associated with conifers, are isotopically heavier than other hydrocarbons. Thus the resin component is a major influence on the bulk carbon isotope composition of some oils. This is especially so for oils containing large concentrations of resin derived compounds (e.g., some from Indonesia which have bicadinane/hopane ratios in excess of 200, see chapter three). Degradative loss of the n-alkanes and isoprenoids from such oils will cause major shifts in the bulk $\delta^{13}C$ values.

7.2.3 Factors controlling the distribution and relative abundance of polycadinene-related compounds

In chapter three, it was shown that the range of values for the bicadinane/hopane ratio in oils is much wider than that for oleanane/hopane, despite the fact that both groups of compounds come primarily from angiosperms. Certainly the bicadinanes have a much more specific phyllogenetic association than the oleananes, but this may not be the sole reason for the wide variation in abundance. As discussed in chapter five, the main source of the bicadinanes is a polymer which remains intact until subsurface temperatures ca. 80 °C are reached. This means that bicadinanes are not subject to the microbially mediated aromatisation reactions which occur during early diagenesis and so their concentration may be more free to vary in response to changes in precursor load. Furthermore, thermal maturity and possibly differential migration phenomena appear to be stronger controls on the relative abundance of bicadinanes than they are for the oleananes. The bicadinanes appear to be among the most resistant hydrocarbons to biodegradation. Hence, they can be used for oil-source and oil-oil correlation even when biodgredation has rendered most other correlation and maturity estimation tools invalid. The bicadinane isomer distribution has proven to be sensitive to thermal maturity prior to and within the "oil window". Maturity indicators based on the bicadinanes and on other compounds derived from polycadinene are therefore useful in assessing the maturity of heavily biodegraded oils. Furthermore, these indicators are less subject to interference from biochemical effects occurring during early diagenesis. Access to a new class of biomarker maturity indicator will help to resolve long-standing questions about the maturity of generation for many Southeast Asian oils.

As predicted by others, minor amounts of bicadinanes have been shown to occur in oils from outside the paleogeographic range of the dipterocarps, confirming the role of other resinous trees (angiosperms ?) in their production. Their presence in Jurassic-age sediments and oils from Australia

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is particularly noteworthy given that dipterocarp fossils have not been found outside Southeast Asia.

7.2.4 Factors controlling the distribution and relative abundance of oleanoid compounds

An observation made in chapter three was that the abundance of oleanane in oils varied less than expected if it were controlled solely by the degree of land-plant input to the source. In particular, oleanane is abundant in some marine carbonate oils even though carbon isotope evidence precludes a significant contribution from land plants. These observations are explained in chapter six in terms of the a) the dominance of aromatisation and skeletal rearrangement processes over reduction where deposition takes place under terrestrial conditions, and b) enhanced generation and/or preservation of olenanes where plant matter comes into contact with seawater during early diagenesis. Hence, there is a hierarchy of factors affecting the abundance of oleanoid compounds in oils:

1.   Age of the source (radiation of the angiosperms during the late Cretaceous/Tertiary)

2.   The relative contribution of land-plant biomass to the source

      and

3.   The efficiency of conversion of 3-functionalised precursors to oleananes as opposed to aromatic and rearranged analogs

Based on an interplay between factors two and three, a model to explain the abundance of oleananes in oils derived from different parts of a deltaic petroleum system has been developed (summarised in Fig. 7.1). Support for this model was found in the oleanane/hopane ratios for a large set of oils (Fig. 6.21, chapter six).

The strong diagenetic control on the preservation of oleananes also means that source rocks deposited in regressive systems tracts should generate oils with higher oleanane/hopane ratios than those deposited in transgressive systems tracts. Again, support for this concept was found in the median oleanane/hopane ratios of oils from different basins. However, even when coals of a transgressive system are the source of oil, marine overprinting during early diagenesis can increase the abundance of saturated oleanoids. Thus, unless sampling is planned in a sequence stratigraphic framework, it would be unwise to rule out a coals as the source of an oil on the basis of a better triterpane match with adjacent shales. Furthermore, the absence of oleanane in an oil or sediment does not preclude a contribution to the source from angiosperms - in the absence of a marine influence it is possible for aromatisation and/or rearrangement of precursor lipids to proceed essentially to completion.

The occurrence and origin of a group of C_{30} "oleanoid triterpanes", one of which has now been identified as a ring A-contracted compound, were discussed in chapters three and six. It appears that these compounds are the products of chemical as opposed to microbial dehydration of precursor lipids and their occurrence in oils derived from acidic peat swamp organics is understandable.

Similarly, the absence of these compounds in oleanane-containing marine oils, where land-plant matter experienced more alkaline conditions during early diagenesis, is readily explained. The ratio of oleanoid triterpanes/oleanane may thus indicate the degree to which the source matter underwent diagenesis in a peat swamp as opposed to marine sediments. However, apart from in the present study, very few measurements of this ratio have been made and no large database comparable to that for oleanane/hopane is available. This is partly because accurate measurement of the oleanoid triterpanes requires a GCMSMS method in order to avoid interference from the C_{29} regular and neohopanes

and the C_{30} diahopane. Nevertheless, the most abundant compounds can be measured using SIM-GCMS methods and ratios involving the recently identified *abeo*-oleanane should now begin to appear in the literature.

Oleanane abundance				
Source environment	**Lacustrine**	**Floodplain**	**Paralic**	**Marine**
Land-plant input	*Moderate-Low*	*High*	*High*	*Low*
Reduction *vs.* Aromatisation	*V.Low*	*V.Low*	*Moderate*	*High*
Leading to oleanane abundance being:	*Low*	*Moderate - Low*	*Moderate - High*	*Moderate*
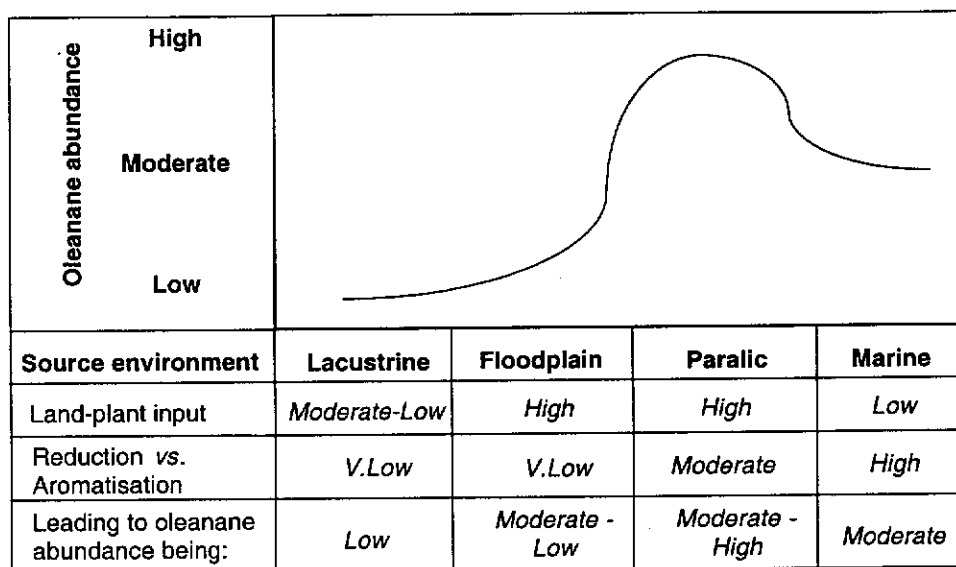
Figure 7.1 A model to explain variations in the abundance of oleananes across a deltaic transect. The model is based on the interplay between supply and diagenetic transformation of precursor tritepenoids.

7.3 Suggestions for further work

Some suggestions for further work are as follows:

7.3.1 Further studies of oleanoid and other compounds as indicators of early diagenetic conditions

It is clear that the major fate of plant terpenoids in terrestrial sediments is aromatisation. Furthermore, much of this takes place during early diagenesis and the extent is sensitive to environmental conditions. Further studies are needed to elucidate the role of sulphur is preserving the double bonds which can be reduced to yield saturated compounds during catagenesis. For example, desulphurisation of the polars from a marine influenced coals and quantitative studies of the any plant terpenoids released would help to

determine the importance of sulphur sequestration as a preservation mechanism. The role of early diagenetic conditions in determining the fate of di- and sesquiterpenoid compounds also needs to be studied. Unpublished work on aromatic compounds in the Maniguin coal has shown that a series of partly aromatised tricylic hydrocarbons are very abundant in the bitumen. The saturated analogs of these compounds, the cheilanthanes, are normally thought of as markers for marine algae or for bacteria that thrive in marine environments (Peters and Moldowan, 1993 and references therein). However, the results for the Maniguin coal suggest that the precursor hexaprenol lipids are present in both terrestrial and marine environments but appear as saturated compounds only in the latter. Further work on the aromatic analogs of the cheilanthanes (which also occur as ring-A opened counterparts) is thus needed.

Further studies are needed to determine the structures of the oleanoid triterpanes which remain unidentified. Also, a much larger database on the concentration of these compounds in oils and sediments needs to be established so that the inferences made in this study can be properly tested. This will require the more general use of GCMSMS methods because the more commonly used SIM-GCMS methods do not provide sufficient discrimination. Nevertheless, much unutilised data exists in the literature and in company reports where the compounds have been labelled simply as "unidentified C_{30} triterpanes or (incorrectly) as "resin derived compounds". Some of these data may be amenable to reinterpretation.

7.3.2 Further studies with bicadinanes as source, maturity and migration markers

This and other recent studies have shown that bicadinanes and related compounds derived from polycadinene can be useful markers of source type, age and maturity. The data presented by Stout (1995) suggest that the cis-cis-trans/trans-trans-trans bicadinane ratio (W/T) depends both on maturity and transport efficiency during expulsion of an oil from coal. Thus a crossplot of W/T vs. BMI-1 for a series of marginally mature coals and shales

might shed light on the timing and mechanism of primary migration. This is an issue of great importance and could be pursued with a suitable set of samples. Furthermore, since the structures of only two of the many bicadinane isomers are presently known, effort should be directed to determining the structures of compounds "T1" and "R" and the other bicadinane and methyl bicadinane isomers. Polycadinene is readily available as commercial dammar resin and it should be possible to prepare a bicadinane concentrate suitable for HPLC or preparative GC separation via pyrolysis and molecular sieving techniques. Hopefully then, the structures of the individual compounds can be determined by NMR and XRD as has been done for compounds T and W. Once standards are available, it will be easier to carrry out quantitative studies of the occurrence of bicadinanes in oils and to search for their presence in oils covering a wider geographic and temporal range. Given their occurrence in Jurassic samples from the Cooper-Eromanga and Perth Basins it seems likely that small quantities of bicadinanes will be found in a wide range of samples. Preparation of pure standards would also allow studies of the mechanism and kinetics of the reactions underlying the bicadinane maturity indicators.

7.3.3 Further studies on the carbon isotope composition of plant resins and resin-derived compounds in oils and sediments

Although this study has provided more data on the carbon isotope composition of resins than previously available, the number, geographic range and temporal range of the samples is still very limited. In particular, only a few samples of well-dated and stratigraphically controlled Class II resinites were available. As discussed in chapter one, there are many factors which can affect the carbon isotope composition of tissues from any given plant. Hence, there must always be a reasonably wide range of $\delta^{13}C$ values for resinites even within a single class. Any conclusions about systematic differences, such as those proposed herein, should be based on as a large a data set as possible. Collection of a larger and more stratigraphically

controlled set of resinites is proceeding and it is hoped that a more complete database of $\delta^{13}C$ values will confirm and refine the trends observed in this study. Resins are fossil materials which are easily identifiable both chemically and petrographically, yield simple compounds found in oils and occur throughout a long geological period from the Carboniferous to the present. A systematic record of carbon isotope compositions would not only aid petroleum geochemical studies but might contribute to knowledge of the changes in atmospheric pCO_2 and $\delta^{13}C$ through time.

Alexander et al. (1992) have effectively used aromatic biomarkers derived from Araucarian conifers in oil-source correlation studies in Australia. One of the limitations of such work is that the characteristic substitution patterns become less apparent at high thermal maturity, due to dealkylation and transalkylation reactions. The present study has shown that conifer derived hydrocarbons have characteristic carbon isotope as well as molecular signatures. This raises the possibility of identifying the Araucarian contribution to an oil via the carbon isotope composition of individual hydrocarbons. Furthermore, this may be possible beyond the point where maturity has caused the disappearance of the characteristic isomer patterns.

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